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SLIDING MECHANISMS FOR GRAIN BOUNDARIES CONTAINING
PRE-EXISTING CAVITIES IN Al_2O_3-SiO_2 CERAMICS

Amar Pal Singh Rana
(Ph.D. thesis)

November 1980

DISCLAIMER

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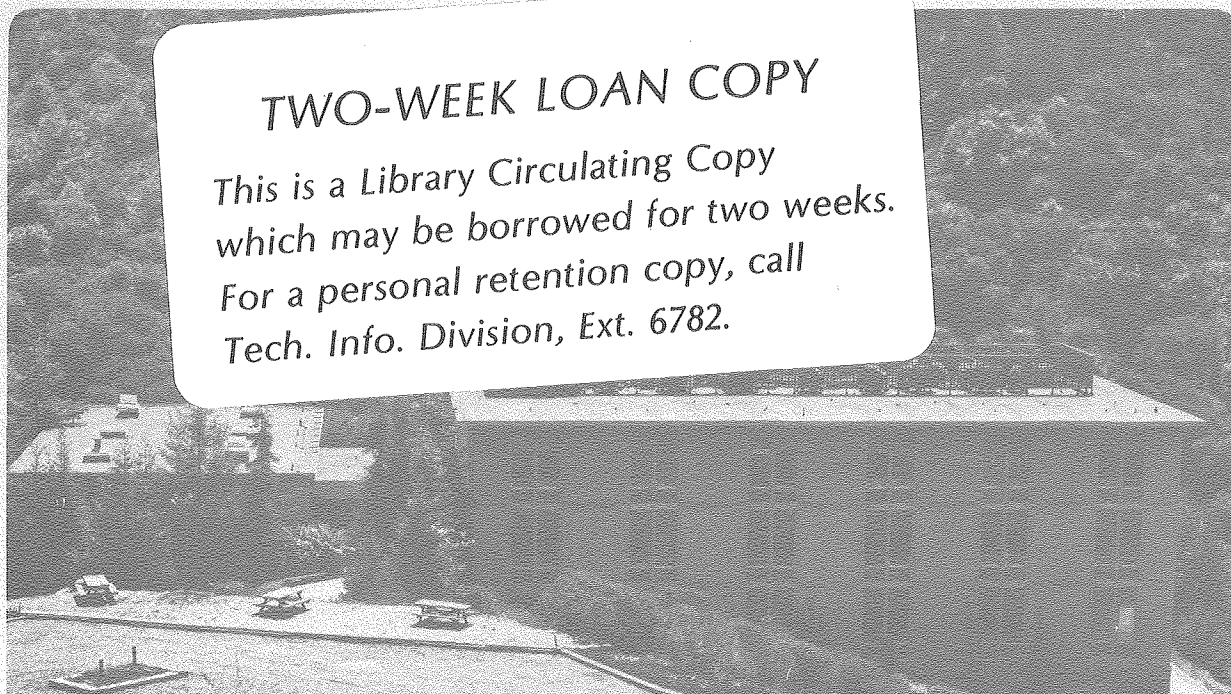November 1980

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ABSTRACT

High temperature failure in ceramics frequently involves the nucleation, growth and coalescence of grain boundary located microcracks or cavities. Fabrication processes such as hot pressing and sintering also lead to the presence of cavities at grain boundaries. The intent of this study is to examine models of grain boundary sliding when cavities are present at grain broundaries in Al_2O_3-SiO_2 ceramics using the internal friction technique.

Internal friction is the dissipation of energy that occurs when stress and strain are not in phase. An apparatus was developed to measure internal friction and elastic modulus up to $1200^{\circ}C$ using a sonic resonance technique, with electromagnetic transducers. In a polycrystal, small amounts of total sliding (strains $\sim10^{-4}$) can be accommodated by elastic strains in the neighboring grains. The sliding is recoverable and is accumulated and discharged with a characteristic relaxation time which is a function of grain boundary viscosity. This relaxation time can be measured in an internal friction experiment.

Models of high temperature deformation in ceramics must recognize the various microstructures that typically occur, particularly the presence of second phases at grain boundaries. Two types of microstructure, and the concomitant modes of grain boundary sliding, were distinguished in this study. The first microstructure consisted of grains encompassed by an amorphous phase. The relaxation time has been calculated when grain boundaries have pre-existing cavities. Sliding in single phase microstructure is accommodated by boundary diffusion and by viscous deformation in materials with a glassy grain boundary phase. Relaxation times derived from internal friction measurements were shown to be in fair agreement with theoretical relaxation times. Cavities only had a small contribution to grain boundary sliding.

At relatively high temperatures, internal friction rises exponentially to very large values. This phenomenon (referred to as the high temperature background) is manifest in polycystalline samples as an upturn in the internal friction on the high temperature side of the peak. A transient analysis pertinent to the high temperature background demonstrated the significance of a dimensionless parameter, which was a function of frequency, grain size, elastic modulus and grain boundary diffusivity.

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CHAPTER 1

INTRODUCTION

Many polycrystals of refractory materials such as alumina, mullite, metallic carbides, etc. are made by sintering at high temperatures. The last vestiges of porosity must often be eliminated if the highest stengths are to be obtained, but this is hard to achieve. There are sufficient observations[1,2] to indicate that high temperature fracture in ceramics frequently involves the nucleation, growth and coalescence of grain boundary located microcracks or cavities. The propagation of individual cavities or cavity arrays, either by diffusion[3-7] or by viscous flow[8] of a boundary phase, is well understood. Coupled cavity propagations and coalescence effects that dictate the final failure have also been examined.[9] The intent of the present paper is to examine models of grain boundary sliding when pre-existing cavities are present at grain boundaries in Al_2O_3-SiO_2 ceramics using internal friction techniques.

In a polycrystal, grain boundary sliding can be accommodated by elastic deformation of the grains. Presence of pre-existing cavities at grain boundaries cause additional sliding. This sliding is recoverable upon removal of applied stress and is accumulated and discharged with a characteristic relaxation time which is a function of the viscosity of the grain boundary in the presence of pre-existing cavities. This relaxation time can be measured in an internal friction experiment.

Models of high temperature deformation in ceramics must recognize the various microstructures that typically occur, particularly the presence and dispersion of second phases at grain boundaries. Two types

of microstructure, and the concomitant modes of grain boundary sliding will be distinguished in the present paper. The first microstructure is one with no second phase at grain boundaries (i.e., a single phase material). Mullite (75 wt.% Al_2O_3) was chosen for this purpose. For this case sliding is accommodated by grain boundary diffusion and the material displaced from pre-existing cavities being accommodated at grain boundaries and vice-versa, causing mode I displacements.

The second microstructure consists of grains encompassed by an amorphous second phase with pre-existing cavities, typical of many ceramics fabricated by hot pressing or sintering. For this case, sliding is accommodated by viscous flow and the material displaced from pre-existing cavities being accommodated at grain boundaries and vice versa causing mode I displacements.

The relaxation time was calculated using a procedure described here in for the two microstructures described. Internal friction experiments were performed to measure these relaxation times. Satisfactory agreement was obtained with the analytic results. The measurements also confirmed the theoretically predicted dependence of boundary viscosity upon pre-existing cavity size and spacing and the grain size.

CHAPTER 2

TOTAL SLIDING FROM ELASTIC ACCOMMODATION

Consider a polycrystal containing pre-existing cavities at the
grain boundaries. When a stress lower than the yield stress is applied
to the polycrystal the following happens: First, there is an instan-
taneous elastic deformation. Second, pre-existing cavities at grain
boundaries cause additional sliding. As elastic boundaries begin to
slide, futher elastic deformation of the grains occur, back stresses
opposing the sliding build up and the sliding comes to a halt. This
is sliding by elastic accommodation.

2.1. Stress Intensity Factor Solutions

The extension of a wedge crack that emanates at a triple point has
previously been analysed using a cracked dislocation solution first
proposed by Stroh[10] and extended by Cottrell.[11] This solution can be
demonstrated to exhibit the form

$$\kappa \, \tau_s \sqrt{1} = \tau_s \, \sin 2\phi \, \sqrt{\pi(a/2)} + \frac{hE}{\sqrt{2\pi a(1-\nu^2)}} \qquad (2.1)$$

where 2h is the wedge opening, a is the crack length, $\kappa (=K/\tau_s \sqrt{\ell})$ is the
normalized stress intensity factor, E is Young's modulus, 2ℓ is facet
length and τ_s is the shear stress at grain boundary. The first term is
due to the normal opening of the crack K_σ and the second derives from
the wedge opening produced by sliding K_w. However, this solution is
inadequate for the complete description of the wedge crack exension;
because the wedge opening h cannot be specified a priori (steady state
sliding will not occur in the present problem). A comparison solution

that provides the requisite complementary information can be derived from recent stress intensity solutions for the kinked crack,[12] with the kink at an inclination $\phi(=2\theta)$ to the sliding boundary Fig. 2-1). The pertinent stress intensity factors are deduced by regarding the primary crack as being subjected to a pure shear stress τ (Fig. 2-1) plus a small superimposed crack surface traction to prevent opening of the primary crack.

The mode I and II stress intensity factors provided by the analysis are then combined in accord with the coplanar strain energy release rate criterion to obtain the driving force K for coplanar wedge crack extension, as;

$$K = \left(K_I^2 + K_{II}^2 \right)^{1/2} \tag{2.2}$$

The results, plotted in terms of the normalized stress intensity factor $\kappa(=K/\tau\sqrt{\ell})$ are shown in Figure 2-1. Rearranging Eq. (2.1), we have

$$h = \frac{\sqrt{2\pi a}\,(1-\nu^2)}{E} \left(\kappa\tau_s\sqrt{\ell} - \tau_s\,\sin2\phi\,\sqrt{\pi(a/2)} \right) \tag{2.3}$$

The average sliding displacement ⟨u⟩ due to cavities at triple points is related to wedge opening h by

$$\langle u \rangle = \frac{\pi}{4}\,h\,\operatorname{cosec}\phi \tag{2.4}$$

Thus

$$\langle u \rangle_{\substack{\text{triple} \\ \text{point} \\ \text{cavities}}} = \frac{\pi}{4E}\,\operatorname{cosec}\phi\,\sqrt{2\pi a}\,(1-\nu^2)\tau_s\left[\kappa\sqrt{\ell} - \sin2\phi\sqrt{\pi(a/2)} \right] \tag{2.5}$$

2.2. Additional Elastic Accommodation

Further we note that the elastic displacement (u) of a mode II crack (length 2ℓ) subjected to uniform shear values with distance x from the center as[13]

$$u(x) = \frac{4\tau_s(1-\nu^2)(\ell^2-x^2)^{1/2}}{\pi E} \tag{2.6}$$

The average displacement is thus;

$$\langle u \rangle = \tau_s \ell (1-\nu^2)/E \tag{2.7}$$

For comparison, we have from Eqs. (2.5) and (2.7)

$$\frac{\langle u \rangle_{tpc}}{\langle u \rangle} = \left(\frac{\pi}{2}\right)^{3/2} \operatorname{cosec}\phi\left(\frac{a}{\ell}\right)^{1/2}\left[\kappa - \sin 2\phi\left(\frac{\pi}{2}\cdot\frac{a}{\ell}\right)^{1/2}\right] \tag{2.8}$$

Which is plotted in Fig. 2-2. It is thus seen that for small values of a/ℓ, typical of experiments, the contribution from triple point cavities is small.

CHAPTER 3

TRANSIENT SLIDING

The total sliding $\bar{U}$ as a result of an applied stress τ_a is given by adding displacements from Eqs. (2.5) and (2.7). Thus we have

$$\bar{U} = \frac{\tau_a \cos\phi \ (1-\nu^2)}{E} \left[1 + \frac{F}{\ell} \cdot \frac{\pi}{4} \ \mathrm{cosec}\phi \ \sqrt{2\pi a} \ \left(\kappa\sqrt{\ell} - \sin2\phi \ \sqrt{\pi(a/2)} \right) \right]$$

(3.1)

where F is a fraction of triple points containing pre-existing cavities. The normal stress σ_n at the sinusoidal boundary of wavelength λ (=3d/2) as a result of applied stress τ_a is given by

$$\sigma_n = - \frac{6\tau_a}{\pi} \ \sin \frac{2\pi}{\lambda} \ y$$

(3.2)

The shear stress across the boundary at time t is given by

$$\tau_s(t) = \tau_a - \frac{2}{\lambda} \int_o^\lambda \sigma_n(t) \ \tan\theta \cdot dy$$

(3.3)

where $\tan\theta$ is the slope of the sinusoidal boundary represented by:

$$x = \frac{d}{2} \cos \frac{2\pi}{\lambda} \ y$$

(3.4)

From Eqs. (3.1) and (3.3) we obtain

$$\tau_s(t) = \tau_a - \beta U(t)$$

(3.5)

where

$$\beta = \frac{2E}{(1-\nu^2)\,\cos\phi\cdot\ell} \left[1 + \frac{F}{\ell} \cdot \frac{\pi}{4} \cosec\phi \sqrt{2\pi a} \left(\kappa\sqrt{\ell} - \sin2\phi \sqrt{\pi(a/2)} \right) \right]^{-1} \tag{3.6}$$

expression for β for fully dense material can be obtained by deleting last two terms in the denominator. Using the equation for boundary viscosity η and taking δ as the boundary thickness

$$\frac{\mathring{U}(t)}{\delta} = \frac{\tau_s(t)}{\eta} \tag{3.7}$$

and combining with Eq. (3.5) leads to

$$\mathring{U} = (\tau_a/\beta - U)\delta\beta/\eta \tag{3.8}$$

The solution to which is

$$U(t) = \frac{\tau_a}{\beta}\,(1-e^{-t/\tau}) \tag{3.9}$$

where the relaxation time

$$\tau = \eta/\delta\beta \tag{3.10}$$

CHAPTER 4

GRAIN BOUNDARY VISCOSITY

In a fully dense material, the characteristic relaxation time is
a function of intrinsic viscosity of grain-boundary. When pre-existing
cavities are present at grain boundaries, the material displaced from
the cavities can be accommodated at grain boundaries and vice-versa
causing mode I displacements. The contribution of pre-existing cavities
is calculated for the two microstructures.

4.1. Single Phase Microstructure

In this case the growth of pre-existing cavities involves grain
boundary diffusion with the material displaced from the cavities being
accommodated at grain boundaries. Such an accommodation mechanism per-
mits only small mode I displacements and small cavity surface separations.

4.2. Continuous Second Phase

Two essentially different mechanisms have been proposed to describe
the growth of grain boundary voids. The diffusive growth models of Hull
and Rimmer[1] and Ballufi and Seigle[2] consider the cavity to be fed by a
flux of vacancies generated in the grain boundary by the applied stress;
the other view has not been quantified but assumes that the cavity
behaves as a shear crack which grows by grain boundary sliding (Gifkins[3]
and Chen and Machlin.[4] Both viewpoints owe their viablity to certain
key experiments which appear to support one mechanism and exclude the
other. Important observations supporting a deformation growth process
are, e.g., the ability of alloying elements to reduce both creep rate
and rupture life whilst having little effect on diffusion (5.6) and the
ability of cavities to grow under a compressive applied stress.[1,8]

The outstanding evidence for the diffusion mechanism is the inhibition of cavity growth on application of hydrostatic pressure equal to applied stress[9]. Evans'[10] approach was to add the total energy of the system in a manner similar to that used by Cottrell[11] and Gilman[12] for cracked dislocation and adapted by Williams[13] for high temperature wedge cracking the cavity was treated as a hollow dislocation. Evans[10] assumed that matrix was sufficiently plastic to accommodate the misfit strains produced during the growth of the cavity. Evans[10] showed that the cavity growth can occur only by grain boundary sliding and that sliding cannot occur without concurrent cavity growth.

Further there is an incomplete amount of evidence (in the opinion of Gifkins[14] in a 1963 review) in favor of the vacancy condensation model, where grain boundary diffusion is the principal path. A number of objections have raised to the model to favor strain-controlled growth. Apart from the early comments of Nield and Quarrel[15] and Chen and Machlin,[16] Kramer and Machlin[17] found that creep strain and void area are linearly related in nickel. This rules out vacancy controlled void growth. Although the creep process itself is reported[18,19] to be dominated in this metal by a vacancy-producing mechanism.

Another objection to vacancy growth originates in the study of Intrater and Machlin.[20] Working in a temperature range of 650° to $900^{\circ}C$, they found that the area of visible voids was independent of temperature. In dilute alloys a linear relation between void volume and strain has been reported by Bowring et al.[6], although Magnox AL 80 the linearity was only achieved late in the creep life. Linearity with creep strain

was also noted by Hensler and Cullen[21] in a series of magnesium alloys. They found the effect to decrease with decreasing grain size.

The effect of pre-existing voids was studied by Davies and Denision[22] who compared samples produced by powder-metallurgical techniques (purposely to contain voids) with fully dense vacuum cast samples of the same material. They showed the time to failure vs strain rate relationship to hold independently of stress and temperature. They went on to assume that creep life had been reduced through an increased creep rate. This results from the presence of voids which drain off any excess vacancies. The results also support those of Kramer and Machlin[17] on the void fraction vs creep strain relationship and reflect the independence of creep rate from vacancy controlled growth.

Gittins[23] pointed out that cavitation rate at high strain rates was probably controlled by grain boundary sliding[24] and at low strain rates by a combination of sliding and vacancy accumulation.[25] In response to these comments, Davies and Williams[26] had shown that vacancy loss can be superceded by deformation controlled growth. They do not accept that a vacancy contribution is significant in cavity growth.

In view of the increasing amount of discussion in terms of a dominant controlling process, attempts have been made to find a transition from vacancy to deformation controlled growth. Day[27] was unable to distinguish between them in steel, nor were Chen and Machlin[16] in their early work with brass. The strain rate-dependent void growth (with respect to tensile axis) found by Gittins and Williams[28] was cited as evidence for such a transition but was criticized, and referred to a change in mode of deformation controlled by Taplin.[29]

A change in control of growth has also been sought by Evans.[30]
Working with a dilute magnesium-aluminum alloy, he concluded that growth
was dominated by grain-boundary sliding. The rate of increase of void
length is directly related to the sliding. The minimum in ductility is
attributed to a maximum void growth rate and its parallel maximum slid-
ing rate. The sliding rate at higher temperatures is decreased by the
formation of grain-boundary cusps. A minimum in the relation between
creep rate and grain size was reported by Wilshire.[31] He found that
it increased as the temperature increased and again discussed the effect
in terms of the increasing importance of grain boundary sliding with
increasing grain size.

The review of Greenwood[32] tends to support vacancy accretion in
the light of experiments involving hydrostatic pressure. However, these
experiments are not without critics. Machlin[33] has given an alternative
explanation. Taplin[34] gives support to the possible role of vacancies
at low strain rates. In contrast Wilshire,[35] writing in 1973, tended to
negate the evidence for vacancy growth because of the results of reversed
stressing experiments. If it is accepted that several mechanisms are
possible, then evidence that vacancy absorption by voids and their result-
ant growth is nevertheless persuasive. Evidence in favor of deformation
controlled growth is far stronger. The non-sphericity of cavities, the
need for tension across the boundaries to avoid sintering, the tempera-
ture independence of void growth, the marked effect of alloying which
does not alter the diffusion coefficient, all can be cited[14,32,34,35]
in support. In addition, the relation between cavitation and creep
strain, and between the rate of change of both and creep life is also

indicative of deformation controlled growth.[35]   Finally there is a good

case to be made for several types of deformation-controlled growth.[34]

According to Hancock,[36] in a creeping solid holes may grow by

vacancy condensation or by the action of the applied stress producing

strains at the surface of the hole which cause it to grow. The latter

mechanism does not involve a vacancy flux to the hole. A comparison

of the two processes indicated the conditions under which hole growth

without vacancy condensation is faster than hole growth by diffusion.

Low values of the ratio $\sigma/\dot{\epsilon}$, where σ is stress and $\dot{\epsilon}$ is the strain

rate as well as large voids favor the strain process.

Several authors have examined the problem of brittle cracking along

grain boundaries during creep.[41-44] These studies have generally com-

menced from the premise that grain boundary sliding will be occurring at

a specified rate, $\dot{u}_{g.b.s.}$, and that the resultant sliding displacements

provide the impetus for extension of a brittle wedge crack.

However, a prescribed steady steady state grain boundary sliding

can only be occurring if the sliding is everywhere acommodated either by

diffusion[45] or, perhaps by cracking. If it is implicitly assumed that

diffusional accommodation is occurring, then it must be appreciated that

diffusion will also modify the configuration of the crack tip.[37-39] In

fact, the crack (which becomes a cavity) will extend by diffusion, in

accordance with the descriptions outlined by Chuang, et al.;[37,40] Vitek[38]

and Speight et al.[39] The earlier models[41-43] used linear elastic wedge

opening solutions to describe the crack length and are thus not pertinent

to conditions which involve diffusion. The presence of a steady state

boundary sliding displacement to extend the crack is thus ambivalent.

It was subsequently recognized[44] that a wedge crack, once initiated, is likely to extend by diffusion, whenever diffusive conditions exist; and an approximate analysis of diffusive extension was presented.

An interesting attempt to produce a model in which both deformation within the grains and vacancy accretion play a role has been made by Ishida and McLean.[48] They envisage dislocations moving down slip lines within the grains to intersect a grain boundary. Under the action of the tensile stress, they migrate along the boundary which can only be done by climb (still retaining their burgers vectors). The vacancies emitted during climb process migrate to a growing cavity. The dislocation also exerts a force on this cavity, tending to open it, which is proportional to the distance between cavities. This model is of particular interest because it relates growth to grain boundary sliding. This model has been invoked to explain experimental observations in dilute nickel and magnesium alloys by Bowrig et al.[6] and in copper and steel by Johannesson and Thölén.[24]

A more detailed analysis based on recent 'crack line' cavity extension concepts[37-39] is needed to afford a thorough description of the failure process. In the present analysis diffusion is not admitted and the only permissible viscous motion is grain boundary sliding. Brittle cracks are then tenable. The occurrence of this condition must be limited (since grain boundary sliding itself usually involves diffusive processes, because of the presence of ledges and of non-planarity), but important situations can be conceived wherein the proposed process might be encountered. For example, ceramics prepared by liquid phase sintering often have planar boundaries, and contain a second phase at the

boundaries. Thus the growth of pre-existing cavities involves mass transport by viscous low with the material displaced from the cavity being accommodated at grain boundary.

CHAPTER 5

THE RELAXATION TIME

The relaxation time which is a function of the viscosity of grain boundary can now be calculated separately for the two microstructures. This relaxation time can be measured in an internal friction experiment.

5.1. Equi-axed Single Phase Microstructure

In this case the relaxation time can be calculated from Eqs. (3.6) and (3.10). Thus we have

$$\frac{\tau \cos\theta}{d \cos 2\theta} = (\eta/\delta) \frac{3(1-\nu^2)}{16E} \quad \frac{1 + 2F \cos\theta \cdot \pi \cosec 2\theta}{d} (\kappa(3d/8\cos\theta)^{1/2}$$

$$- \sin 4\theta (\pi a/2)^{1/2}) \tag{5.1}$$

5.2. Continuous Second Phase

In this case the relaxation time can be calculated from Eqs. (3.6) and (3.10) and we get Eq. (5.1).

CHAPTER 6

EXPERIMENTAL METHOD

6.1. Materials

The Al_2O_3-SiO_2 system is probably the most important in ceramic technology due to the abundance and wide spread use of alumina, silica, and alumina-silicate materials. Mullite, the only intermediate compound stable at high temperatures and normal pressures, is a commonly occurring phase in refractories, whitewhares, and porcelains. Recent studies, with single crystal and high purity, high density polycrystalline mullite, have shown that only a fraction of mullite's potential capabilities, in regards to mechanical strength, creep resistance, and acid corrosion resistance are achieved in normal processing.[1-6] Potential applications of improved mullite-containing ceramics are refractory materials for coal gasifiers vessels,[6,7] random materials,[8] and high temperature structural materials.

Many methods have been used in forming mullite, from high temperature decomposition of naturally occurring alumino-silicates (such as clay minerals) to chemical preparation techniques involving high pruity raw materials. Several reviews of these methods are available,[4,9,10] however, on the sintering behavior of mullite-containing materials.

Several studies have been made on the kinetics of hot pressing of mullite.[2,11] Referring to Al_2O_3-SiO_2 phase diagram (Figs. 6-1 and 6-2) we notice that mullite with 75 wt.% Al_2O_3 presumably has no glassy phase at grain boundaries. Thus this composition was chosen for the single phase microstructure. For a microstructure with a continuous film of

glassy phase and pre-existing cavities at grain boundaries, a composition with 71.8 wt.% Al_2O_3 (mullite) was chosen.

There is a wide selection of Al_2O_3 and SiO_2 available. The starting materials in this study were A-14[*] aluminum oxide (α-alumina) and silica flour[†] (α quartz) which had purities of 99.8% and 99.6% respectively. Semi-quantitative spectrographic analyses[§] (Table 6-1) shows that the major impurity in A-14 was SiO_2 and the major impurity in the silica flour was Al_2O_3. Mixing and de-agglomeration were achieved by wet (isopropyl alcohol) milling in a teflon lined vibratory mill.[||] After stir drying and screening (-120 mesh) mixtures were calcined at 1650°C for 48 hours to form mulllite. Reaction is considered complete when no α-Al_2O_3 was detected in X-ray diffraction pattern.[¶]

After calcination, mixtures were subjected to coarse crushing in a mechanically operated mortar and pestle[**] and wet (isopropyl alcohol) vibratory milling. The grinding time was 3 hours. After stir drying and screening (-120 mesh) powders were calcined at 600°C for 1 hour to volatalize any organic contamination. Powders were labeled according to composition. X-ray diffraction and microscopy have shown the most significant contamination in processing to be α-Al_2O_3 introduced by impact collisions during milling (high density alumina grinding media[††] were used).

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[*]Alcoa, Aluminum Corp. of America, Bausite, Arkansas
[†]Ottawa Silica Co., Ottawa, Illinois
[§]American Spectrographic Laboratories, Inc., San Francisco, California
[||]Sweco, Inc., Los Angeles California
[¶]Norelco Diffractometer, Philips Electronics Instruments, New York
[**]Pulverisite, Alfred Fintsch Co., Germany
[††]Norton, Co., Akron, Ohio
[††]Coors Porcelain Co., Golden, Colorado

Table 6-1. Spectrographic Analysis of Raw Materials**

	Alcoa A-14	Ottwa Flour
Al	Principal Constituent	0.2%
Si	0.035%	Principal Constituent
Na	0.02	0.02
Ca	0.02	0.02
Mg	0.001	0.035
K	0.5*	0.5*
Ti	0.005	0.025
Fe	0.03	0.05
Ga	0.01	---
Cu	0.001	0.001
Mn	0.001	0.001
Zr	0.01	0.003
Cr	0.001	0.001
Ba	---	0.004
Zn	---	---
B	0.01	0.01
Pb	---	0.005
Ni	---	0.001
Sr	---	0.005

The above are reported as oxides of the elements indicated.

*0.05% was detection limit

**American Spectrographic Laboratories, Inc. San Francisco, California

6.2. Vacuum Hot Pressing

Pressure sintering was performed for the case of single phase micro structure on small batches of pre-reacted mullite (75 Wt.% Al_2O_3) powder in a graphite die at temperature of 1550°C and 500 psi. The die had a 3" diameter bore and the plungers fit loosely to accommodate grafoil lining on the walls and plunger faces. After a powder charge was loaded and tamped, the assembly was cold pressed to an estimated density of 30% of theoretical. The die assembly as shown in Fig. 6-3 was heated at a rate of 400-500°C/hr to 1500°C as read from the Pt-Pt10% Rh thermocouple within the die. Pressure was exerted by virtue of the vacuum of the furnace changer design such that the powder compact was always under a pressure of 15 psi. At 900°C, 250 psi were applied externally. The external pressure was doubled at 1300°C and maintained throughout the balance of the cycle until the die had reached room temperature. The coefficient of expansion of graphite exceed that of mullite causing a hoop stress on the hot pressed disc as it cooled. Maintaining the pressure during cooling assured the integrity of the piece. The temperature was held at 1550°C for 1 hour and then allowed to cool at 400°C/hr until 1000°C at which time the furnace was turned off. Throughout the experiment the ram motion, vacuum, and temperature were recorded. Afterwards the expansion/contraction, rate thereof, temperature and vacuum were plotted simultaneously against time. The hot pressed disc was removed from the die.

A transmission electron micrograph of mullite (75 wt.% Al_2O_3) is shown in Fig. 6-2 at a magnification of 28,000X. This figure shows equilibrium dihedral angles indicating the absence of a second phase

at grain boundaries. Scanning electron micrographs of same composition but with cavities present is shown in Fig. 6-4 a and b. To generate a microstructure with a continuous film of glassy phase at grain boundaries along with cavities, a pre-reacted powder with 71.8 wt.% Al_2O_3 and 28.2 wt.% SiO_2 was hot pressed as described above to a maximum temperature of $1500^{o}C$ with 100 psi external pressure applied. This gave a disc of 3" diameter and 1/8" thickness. Transmission electron micrograph showing acute dihedral angles and glassy phase at grain boundaries is shown in Fig. 6-5(a) and scanning electron micrograph with cavities at grain boundaries is shown in Fig. 6-5(b). After hot pressing, the samples were cut using a diamond blade and heated to $900^{o}C$ for 4 hours to oxidize any carbon picked up from dies during hot pressing and then ground to a final size of 6.5 by 0.8 by 0.25 cm with faces of the bars flat and parallel and parallel to within $\pm$ 0.002 cm. Such precision was necessary to obtain correct values of the elastic modulus. After testing these samples, they were heated to $1750^{o}C$ for 6 hours in Brew[*] furnace and tested again.

6.3. Properties

X-ray diffraction was performed under the following conditions: Scanning conditions were 40 kV, 20 mA, 1°/min, 1/4/1 entrance to exit collimation, time constant 3.0 and range $3*10^{3}$ cps. High intensity copper K X-rays were used. In the single phase microstructure, mullite was the only phase detected. In the microstructure with a continuous film of glassy phase mullite was the only phase detected. No quantitative measurements of peak intensities were made. The descriptive assess-

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[*]Brew, Concord, New Hampshire

ment of intensities were based on visual comparison of the heights for the strongest peak for each case.

Ceramographic polishing procedure consisted of grinding on (1) 200, 30, 15 and 6 micron metal bond diamond wheels. This was followed by vibratory polishing* using slurries of 6,1 and 1/4 micro diamond paste[†] and oil. Samples were observed by scanning electron microscopy.[§] A light etch with diluted hydrofluoric acid solution for the case of sample with a continuous film of glassy phase and a thin (~200 Å) gold coating was sometimes needed to bring out features.

For the case of single phase microstructure, the polished samples for viewing by SEM were thermally etched (1350°C) in order to make the grain boundaries visible. Etching was followed by coating with a thin gold layer. In order to determine average grain size, photographs were placed underneath a transparent plastic sheet, on which parallel lines had been drawn. The grain size was obtained by counting the number of grain boundaries intercepting straight lines of known length. Corrections for the presence of porosity were made according to the method of Wurst and Nelson.[12] Magnification and statistical (multiplication by 1.56) corrections were also made. Results are given in Table 6-2. Fraction, F, of triple point containing these cavities were also determined for the two microstructures and is given in Table 6-2.

Table 6-2. Physical properties of the two microstructures

Properties	Single phase microstructure	Continuous glassy phase
grain size (d) μm	2.5	2
a (μm)	0.4	0.3
F	0.5	0.4

6.4. Modulus of Elasticity Measurements

Simple elasticity theory assumes that the stresses and strains in structural members are uniquely related to one another through the proportionality constants called the elastic constants. If the elastic constants of the material are known, the strain components may be calculated from the stress components or vice versa. For most engineering work it is assumed that the material is elastically isotropic. It is then necessary to define only two elastic constants, one relating normal stresses and strains and one relating shear stresses and strains. One is known as Young's modulus of elasticity and the other as the shear modulus.

There are two methods of determining values of Young's modulus—static and dynamic. In general, the dynamic method is capable of giving precise values without destruction of specimen and is more convenient than the static method. In addition, particularly at elevated temperatures, the static method introduces "anelasticity" (dependence of elastic deformation on time) and thus gives 'relaxed' modulus of elasticity. On the other hand, an instantaneous deformation on application of stress

defines 'unrelaxed modulus of elasticity.' Various equations[13-15] have been derived to express the vibration of a bar-shaped specimen, all of which are approximate, utilizing correction terms to account for the individual modes of the vibration. The Young's modulus can be obtained from the transverse fundamental frequency as follows[16]

$$E = 0.96478*10^{-8} \frac{P}{b} \left(\frac{L}{a}\right)^3 F_1^2 \qquad (6.1)$$

where E is the Young's modulus in kg.mm-2, P is the weight of sample in gms, L is length (cm), b is width (cm) and 'a' is thickness (cm), F_1 is the fundamental transverse frequency. Greater accuracy in the calculation of E is obtained when effects of shape, size and Poissons ratio are taken into account. The elastic modulus was calculated from this value and the dimensions and mass of the specimen. Use of tables published by Hasselman[17] considerably reduced the calculation time.

At an elevated temperature, the value of Young's modulus, E_t, can be calculated using E_0 at room temperature as reference and the resonant frequency at temperature, T, providing allowance is made for the thermal expansion of the material.[18] Thus,

$$E_t = E_0 \left(\frac{f_t}{f_0}\right)^2 \left(\frac{1}{1+\alpha.\Delta T}\right) \qquad (6.2)$$

where α is the thermal expansion coefficient and ΔT is the difference between temperature T and room temperature. The quantity α may be obtained by dilatometer. However, in most ceramic materials, the quantity can frequently be ignored because of its low value.

6.5. Internal Friction Measurements

The internal friction of a solid material usually refers to 'damping capacity' and is a measure of its rate of self-absorption of vibrational energy. This is essentially the conversion of the vibrational energy into heat and the subsequent loss of the heat. In vibratory motion, the damping is characterized by a decrease in amplitude with time for instantaneous shock vibration, the damping causes a limitation of the maximum amplitude. This effect is usually observed as the sharpness of the peak in a resonance curve for low-damping solid materials and the broadness of the peak for high-damping solid materials.

It is well recognized that a measurement of the internal friction is a more sensitive method of studying 'anelastic' behavior of materials than is the measure of elastic constants. Because of the anelastic behavior of materials, the applications of harmonic vibrations leads to a phase difference between stress and strain and, consequently, a loss of vibrational energy which results in damping of mechanical vibrations. Therefore by using different modes of vibrations, at low or high stress, changes in state or condition can be followed without destruction of specimen, or changing any of the variables of the system. Hence, it is possible to study, with a single specimen, phenomena of recrystallization, of phase changes, of structural changes, and of other physical changes.

Several methods have been utilized by various investigators which are briefly reviewed below:

Method 1: When the damping capacity of a material is sufficiently high to give a detectable hystersis in plots of static stress-strain curves, the area of the hystersis loop divided by the work of deformation is a measure of the corresponding internal friction.

Method 2: Providing the damping of a material is sufficiently high to give a detectable variation, the material can be periodically stressed at constant maximum amplitude, when the rate of temperature rise or energy input is a measure of internal friction of the material.

Method 3: When the damping is sufficiently high, say 10^{-2} or higher, measurement of heat loss under the steady state condition with periodic stressing can be correlated to internal friction.

Method 4: When the damping is sufficiently high, the energy required to sustain a periodic vibration may be measured and used as a measure of internal friction. The greatest difficulty experienced in this method will be losses in the electrical system due to the electronic hystersis.

Method 5: When the damping is sufficiently high, a lateral deflection of a rotating shaft having a fixed mass at one end has been used as a measure of the internal friction.

Method 6:   When a known torque is applied to the specimen and then

released suddenly, a measure of the rate of amplitude

decay of free vibrations can be used to measure internal

friction. High stresses may be easily attained by this

method, but low stress measurements are difficult to

detect and record. During these measurements, changes

in the state of material may be followed (due to the

high stress). With an appropriate means for measuring

the rate of decay, either high or low damping materials

may be studied.

Method 7:   Under a continuous vibrational process, where a specimen

is freely suspended at either end near the node of the

vibration, a measure of variation in amplitude of forced

vibrations as the frequency is varied about a resonant

frequency, can be used to determine internal friction.

This is known as the resonance method and recently became

popular with many investigators in the general field of

solid state and particularly for ceramics.

In the present investigation, the resonance method was selected

because this method provides (a) direct means of measuring the damping

capacity, and (b) wide range measurements of the damping capacity up

to fairly high temperatures (about $1200^{\circ}C$).

Internal friction measurements can be made by interrupting the

excitation to the sample and counting the number of cycles it takes for

the amplitude of oscillations of the sample to decay from a reference

amplitude to 1/e of this amplitude. In our case, internal friction

was measured by 'width at half maximum' of the resonance curve. The value was obtained by locating the resonant frequency (at maximum amplitude) and then locating the two frequencies above and below the resonant frequency at which the amplitude decreased to half of the resonance amplitude. Internal friction is then obtained from the difference of the two frequencies and the resonant frequency by[16]

$$Q^{-1} = 1.8136 * \frac{F}{F_0} \tag{6.3}$$

In the dynamic measurement of Young's modulus and internal friction, the specimen is part of the vibrating system. Young's modulus was obtained using a sonic method pioneered by Forster[19] and further explained by Spinner and Tefft.[20] A block diagram of the apparatus* is shown in Fig. 6-6. Such a system has a measuring range from 600 to 25,000 Hz, and provides for the standard off-the-shelf components. The system consists of (1) a driving circuit, (2) a pickup circuit, and (3) specimen support. In the driven excitation mode, the variable frequency oscillator supplies a driving voltage to the sending transducer. The transducer converts the electrical oscillations into mechanical oscillations and couples them to the sample. At the other end the mechanical vibrations of the sample are converted to electrical signals by the receiving transducer. These electrical signals are amplified and their amplitude is indicated on the meter and displayed on the oscilloscope screen.

The amplified signal is also applied to the counter unit which counts the frequency. If the signal is too weak to operate the counter

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unit, there is provision to connect the counter unit directly to the variable frequency oscillator instead of the amplifier. In this case the counter counts the number of cycles per second of the oscillator directly. In the self-excitation system, the feed back amplifier in connection with the sample and transducers forms an oscillator circuit. The frequency of oscillations is determined by the resonant frequency of the sample. The receiving transducer is connected to a second amplifier which feeds the signal into the metering circuit and the oscilloscope circuit. The frequency counter counts the number of cycles per second of the frequency. A disadvantage of this method of excitation is that the frequencies excited will be those most suitable for the feedback conditions existing. It is, however, worthwhile to experiment with the coupling or the phase adjustment to get proper excitation. Once this correct adjustment is found, very exact and convenient measurements are possible which do not require frequency or amplitude readjustments, even in cases where considerable changes in moduli or damping occur.

6.5a. Identification of the Vibrating Mode

As described previously, there are three types of vibrations normally excited, namely, flexural, torsional, and longitudinal. Besides, a rectangular bar has two types for any mode of flexural vibration, depending upon the relation of the direction of vibration to either cross sectional dimension. If the vibration is parallel to the short side of the cross section, it is generally called 'flatwise' flexural vibration; and if it is parallel to the long side of the cross section, it is called 'edgewise' flexural vibration. In order to calculate the

elastic moduli of the specimen, one must know exactly the type and mode
of the vibration.

As the scanning frequency approaches the resonance frequency of
the specimen, a Lissajous pattern appears on the oscilloscope. The
frequency at which the maximum amplitude is observed is the resonance
frequency. Since the Lissajous pattern, whose shape is controlled by
the phase shift of the electronic signal, is an exact reflection of the
mechanical vibration, it is possible to determine whether the motion
of the specimen at the position of the driver and the pickup is of the
same phase or opposite. When the Lissajous pattern is adjusted so that
the direction of the diagonal is down to the left for the same phase,
there will be no pattern at the nodes and a down-to-the right direction
will occur for the opposite phase, as shown in Fig. 6-7.

By counting the number of nodes along the bar, one can determine
the mode of vibration. Torsional modes gave the change in pattern along
the cross-sectional face of the bar, as shown in Fig. 6-7. Except for
some specimens which have an unusually low shear modulus, the fundamental
torsional resonant frequency for thin rods or bars is higher than the
fundamental flexural resonant frequency. The fundamental flexural vibra-
tion has two modes. The fundamental torsional vibration has only one
node at the center. If one observes a resonant condition which has a
node at the center, after observing the resonant condition with two
nodes, one can anticipate that it is the torsional vibration.

An alternative approach is to identify the mode of vibration from
the position of the nodes. Torsional vibrations give the same nodal
position; the fundamental having a node at the center, and the first

overtone at 0.251 and 0.751 from one end of the specimen. Flexural vibrations give slightly different nodal positions, which are 0.2241 and 0.7761 for the fundamental mode. These nodal points can be made visible by placing a find substance such as SiC powder on the specimen, as suggested by Hasselman;[17] the grains will then accumulate at the position of the node. Measurements of internal friction with the Forster-type apparatus are complicated by energy loss and by resonances in the apparatus. At room temperature, the energy loss can be minimized and the true value of the internal friction can be determined. It is very laborious to make measurements at elevated temperatures because the internal friction of polycrystalline refractory oxides characteristically increases with increasing temperature to the point that the electrical noise level caused by resonances in the supporting wires is comparable to the amplitude of vibration of the specimen. For these measurements, particular precautions must be exercised, a few of which are as follows:

1) The size of suspension wires is critical. This is because the suspension wires themselves may sometimes be in resonance at some frequency near the resonant frequency of the specimen. This precaution requires special attention at elevated temperatures where energy losses of specimen become greater. The best solution is by trial and error, using different sizes and types of wires.

2) At elevated temperatures, the oxidation characteristics of the suspension wires demand consideration. When the oxidation reaction takes place on the wires, this seems to create excessive noises, possibly due to the effect of energy dissipation around the wires, which is difficult to separate from the noise of mechanical origin.

Forster in his original paper[21] showed that with light specimens, it is necessary to keep the suspension near the nodes (suspension wires are also used for excitation and as vibration probe) of the sample or values of Q^{-1} much higher than true values may be obtained because of damping by suspension. Especially for low values of Q^{-1}, the effect of damping by suspension is very important; values of Q^{-1} in error by an order of magnitude may be obtained if this damping is not eliminated.[22] The suspension damping can be reduced by moving the suspension near the nodes, but the suspension must be some distance away from the nodes in order to function as driver and as pickup. The practical question is as to whether both requirements can be satisfied at once, i.e. whether the suspension can be far enough from the nodes to permit effective driving and pickup and yet close enough to reduce support damping to an appreciable level. Thus a method of measuring specimen vibration which would be free from this difficulty was sought at kilo hertz frequencies.

6.5b. Suspension System

To avoid the above mentioned difficulties the specimen rested exactly at nodes on alumina rods and the sample was coupled to transducers by Pt + 40 wt.% wire (0.005" diameter) at the ends by drilling holes at diagonally opposite corners and using alumina cement. This means of coupling has the advantage that excitation of all three modes of vibration, transverse, torsional and longitudinal, and their respective harmonics are possible. The suitable placement of the wire contact will always produce a component to produce the desired mode of excitation. It also gives sufficient mechanical decoupling between the test rod and transducer to eliminate additional damping during

internal friction measurements. The disadvantage of the wire coupled system is that the degree of coupling is not defined. It is a function of wire direction and tension and in case of very unfavorable conditions, a function of the amplitude of vibration.

6.5c. Transducers

The conversion of electrical into mechanical energy is accomplished by transducers. Piezoelectric transducers undergo phase transformation and/or loose water of crystallization with temperature. Electrostatic transducers pick up induced field from furnace heating elements, etc. and electromagnetic transducers were used for ceramic samples after some modification. The electromagnetic field acts on a thin membrane consisting of 0.005" steel shim stock. A wire of 0.005" diameter constituting of Pt with 40 wt.% Rh, is spot welded at the center of the membrane. This wire transmits vibration to and from sample for driver and pickup transducers respectively.

The electromagnetic transducers contain a permanent magnet which produces a magnetic D.C. field in a yoke. An A.C. field of suitable frequency is superimposed into the D.C. field. The vibrating force on the membrane will be proportional to this field as long as this peak to peak value does not exceed the D.C. field. When the excitation and resonance frequency coincide, the specimen will oscillate. At the pickup transducer, the coupling wire vibrates the shim stock. As the distance between the shim stock and transducer varies during vibrations of the specimen, a voltage is induced in the windings which is of equal frequency. In order that direct electromagnetic coupling between the transducers may be avoided, the laminations of each transducers must be

3. Minimizing noises due to acoustic and static radiations which
   usually originate from the heating elements used. In this
   respect resistance heating elements rather than induction type
   are desirable and were used.

To meet the above specifications, a vertically split two piece
furnace was used for the investigation of specimens at temperatures
up to $1200^{\circ}C$ as shown in Fig. 6-8. The furnace was constructed such
that the electrical heating elements in the two positions completely
surrounded the test compartment. The sample rests on two small alumina
rods mounted on two D-shaped alumina supports which can be adjusted
to place sample at nodes. The assembly is so chosen that the center
of the sample coincides with the center of the furnace. As described
earlier, electromagnetic transducers are used in conjunction with a
special ferro-magnetic disc mounted on transducers. This disc rotates
and the vibrations are conveyed to sample and vice-versa (receiver)
through excitation wires (Pt + 40 wt.% Rh and 0.005" diameter) spot
welded to center of these discs. Nonmagnetic spacers are used to adjust
distance of the disc from electromagnetic transducers. At the beginning
of high temperature experiments, the transducer mounting device should
be adjusted so that the thermal expansion of the sample can be compen-
sated by means of fine adjustment screws. The adjustment screws are
first completely turned in, then as the temperature increases, the
couplings are slightly tightened from time to time. In this manner an
optimum condition of energy transfer is maintained. This operation is
reversed when the temperature decreases to compensate for thermal con-
traction. The temperature was controlled using a Pt + 10 wt.% Rh

positioned so they are mutually perpendicular. Further all electrical leads should be well coiled to avoid extraneous electric/magnetic field pickup by transducers.

The most favorable conditions are obtained when the coupling wires are slightly bowed and flexible when pressing against the test rod. The most suitable mechanical coupling can be selected with the aid of two fine adjustment screws (Fig. 6-8) after the resonant frequency or its vicinity has been arranged. In order to prevent the wires slipping from test rod, small holes are drilled at the two ends of the sample diagonally apart and coupling wire attached by means of alumina cement. These transducers are identical and can be interchanged. The following are the electrical characteristics of the transducers:

Copper resistance : 150 ohms

Inductance   : 100 mH

Maximum current   :   40 mA

6.5d. High Temperature Measurements

Measurements of elastic constants and internal friction by dynamic method, at elevated temperature requires means of:

1. Obtaining a known uniform temperature over the length of a specimen,

2. Controlling this temperature during the process of a measurement, and

thermocouple and is measured via another Pt + 10 wt.% Rh thermocouple placed in the center of the specimen chamber. This set up is equally good for any atmosphere including vacuum.

A linear temperature dependence has been observed[23] for Young's modulus of several polycrystalline refractory oxides including aluminum oxide, magnesium oxide and thorium oxide above room temperature with the exception of a rapid reduction from linearity occurring at high temperatures. In Figs. 6-9, 6-11, 6-13 and 6-14, and Tables 6-3 to 6-8, the initial linear decrease in modulus above room temperature is due to thermal vibrational energy increasing the separation between atoms and slightly decreasing the force necessary for further separation. For a given frequency, a temperature will be reached where grain boundaries start becoming mobile resulting in relaxation of shear stresses acting on grain boundaries, and the elastic modulus will start decreasing rapidly. Beyond the temperature (T_p), corresponding to the peak in internal friction, Q^{-1} vs temperature (Fig. 6-10), the boundaries become sufficiently mobile and the shear stress along the grain boundaries is essentially relaxed at all times. Thus the rapid drop stops, whereas the linear drop due to thermal vibrational energy continues.

The drop in elastic modulus M, due to anelastic relaxation only (grain boundary relaxation) is given by[24]

$$M - M_r = \delta M \left(\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right) \qquad (6.4)$$

Where M is elastic modulus, M_r is relaxed elastic modulus, δM is relaxation of the modulus, ω is frequency and τ is relaxation time.

Table 6-3. Data on commercial Al_2O_3 (3.599 $g.cm^{-3}$, 4200 c/s)

T^oC	$E*10^{-3}$ $Kg.mm^{-2}$
97	29.91
399	28.92
576	28.37
649	28.41
698	27.77
788	27.52
901	27.41

Table 6-4. Data for Al_2O_3 + 1.5 wt.% SiO_2

T^oC	$E*10^{-3}$ Kg.mm^{-2}	$f_r(c/s)$	$\Delta f_r(c/s)$	$Q^{-1}x10^3$
24	26.21	5076	2.88	1.028
500	24.85	4941	3.06	1.124
550	24.56	4912	3.09	1.141
681	24.35	4891	3.56	1.321
693	24.12	4868	3.62	1.349
711	24.16	4872	4.19	1.561
723	24.11	4867	4.76	1.774
734	24.06	4862	4.86	1.813
742	24.01	4857	4.75	1.773
747	23.89	4845	4.67	1.748
756	23.82	4838	4.59	1.721
762	23.78	4834	4.13	1.549
777	23.71	4827	4.12	1.547
787	23.76	4827	3.93	1.474
795	23.47	4830	3.95	1.483
831	23.64	4819	3.80	1.431
972	23.21	4775	6.06	2.301
1009	23.01	4755	6.88	2.623
1012	22.96	4750	6.81	2.601
1016	23.06	4760	7.55	2.876
1040	22.97	4751	8.65	3.301

Table 6-5. Data on 97.5 wt.% Al_2O_3 + 2.5 wt.% SiO_2

T^oC	$E*10^{-3}$ $Kg.mm^{-2}$
373	22.00
473	21.65
571	21.30
606	21.17
773	20.60
871	20.29
923	20.06
953	19.96
969	19.88
981	19.77
988	19.66
996	19.65
1009	19.63

Table 6-6. Data on 71.8 wt.% Al_2O_3 sample (mullite, porosity = 32%)

T^oC	f_r(c/s)	$E*10^{-10}(N/m^2)$	Δf_r(c/s)	$Q^{-1}*10^4$
241	14,560	13.69	2.52	3.14
317	14,501	13.58	2.48	3.10
439	14,437	13.46	2.53	3.18
667	14,265	13.14	3.00	3.81
682	14,232	13.08	3.17	4.04
711	14,210	13.04	3.31	4.22
722	14,199	13.02	3.47	4.43
729	14,205	13.03	3.74	4.77
737	14,177	12.98	3.65	4.29
744	14,156	12.94	3.89	4.98
753 (T_p)	14,166	12.96	3.94	5.04
772	14,128	12.89	3.52	4.52
780	14,079	12.80	3.81	4.91
813	14,035	12.72	3.23	4.17
827	14,013	12.68	3.43	4.44
850	13,890	12.46	3.48	4.54
872	13,829	12.35	4.00	5.25

Table 6-7. Data on mullite (75 wt.% Al_2O_3, porosity = 28%)

$T^\circ C$	f_r(c/s)	$E*10^{-10}(N/m^2)$	Δf_r(c/s)	$Q^{-1}*10^4$
192	16,157	15.93	---	---
704	15,829	15.29	---	---
751	15,803	15.24	2.08	2.39
796	15,798	15.23	2.09	2.40
817	15,783	15.20	2.10	2.41
834	15,772	15.18	2.11	2.43
850	15,741	15.12	2.18	2.51
866	15,730	15.10	2.22	2.56
895	15,715	15.07	2.35	2.71
909	15,678	15.00	2.41	2.79
916 (T_p)	15,647	14.94	2.91	3.37
921	15,626	14.90	2.59	3.01
924	15,616	14.88	2.56	2.97
933	15,626	14.90	2.45	2.84
941	15,584	14.82	2.41	2.80
950	15,574	14.80	2.47	2.88
959	15,558	14.77	2.54	2.96
970	15,563	14.78	2.66	3.10
986	15,542	14.74	2.77	3.23
1044	15,489	14.64	---	---

Table 6-8. Data on 71.8 wt.% Al_2O_3 sample (mullite)

$T^{o}C$	$f_r(c/s)$	$\Delta f_r(c/s)$	$Q^{-1}*10^4$
217	4061	1.31	.584
476	3976	1.43	.650
608	3959	1.55	.709
647	3935	1.64	.755
665	3936	1.64	.754
703	3920	1.91	.882
731	3907	2.16	1.002
752 (T_p)	3903	2.39	1.110
768	3882	2.15	1.005
769	3874	1.94	.907
775	3868	1.97	.922
782	3872	1.87	.876
802	3858	1.96	.921
805	3850	2.03	.955
831	3843	2.10	.991
905	3800	3.19	1.523
958	3788	4.37	2.091
992	3762	5.17	2.492

By substituting $x = \ln\omega\tau$, Eq. (6.4) reduces to:

$$M-M_r = \frac{\delta M}{2} (1 + \tanh (S+U/T))$$ (6.5)

Wachtman et. al.[25] have suggested an empirical expression for temperature dependence of elastic modulus for temperatures approaching absolute zero to sufficiently high temperatures before departure from linearity occurs in polycrystalline samples due to grain boundary slip.

$$M = M(0) - B*T* \exp(-T_o/T)$$ (6.6)

where M(0) is value at absolute zero and is approached with zero slope as required by the third law of thermodynamics. At high temperatures $\exp(-T_o/T)$ approaches unity and the equation gives a linear dependence with temperature. This was given a theoretical basis by Anderson[26] in terms of a corresponding equation for bulk modulus. From Eq. (6.5) and (6.6), for polycrystalline materials above room temperature this can be described by:

$$M(T) = M(0) - C*T - F(1 - \tanh (S+U/T))$$ (6.7)

where M(T) is the elastic modulus at temperature T K, M(0) is the extrapolated value to 0 K of linear drop due to thermal vibrational energy, C is the slope of the linear decrease due to thermal vibrational energy, and F is the drop near T_p. For a material with single relaxation time (τ), $S = -U/T_p$ where U = Acitivation energy/gas constant. Though this equation is strictly true in the region of the internal friction peak and for a unique relaxation time, the form of the equation is also valid

for a distribution of relaxation times as shown in Fig. 6-12 and Table
6-5 for grain boundary relaxation in a specimen of Al_2O_3 with 2.5 wt.%
SiO_2. The rapid drop due to grain boundary sliding is quite significant.
In the case of distribution of relaxation times the equation was fitted
by adjusting the parameter U. This distribution of relaxation time
occurs when only a fraction of the boundaries are in a condition to
relax near T_p. Some already relax easily while others are still stiff.
This is quite obvious from Fig. 6-12 and Table 7-1. A lognormal distri-
bution in relaxation times was used to adequately describe the spectrum
of relaxation times governing the grain boundary relaxation with distri-
bution parameter of 3.25. A theoretical single relaxation time curve
is also shown. An activation energy of 160±20 Kcal/mole was found by
peak shift due to change in frequency. This agrees well with literature
values.[27-29]

Chang[30] in working with nominally pure polycrystalline Al_2O_3 found
an internal friction peak at about 1100^oC (~7 c/s). Wachtman[31] found a
peak at 1200^oC (~1 Kc/s) whereas Crandall[32] found a peak at 1080^oC
(~5 Kc/s). No special microstructural analysis was done concerning
the microstructure of test specimens. Additions of small amounts of
Cr_2O_3 or La_2O_3 gave rise to a peak around 850^oC as found by Chang[30]
who obtained an activation energy of 47 Kcal/mole for the peak due to
Cr_2O_3. He suggested that marked decrease in activation energy when
small amounts of Cr_2O_3 was added can be understood by assuming that a
smaller numer of atoms are disordered during grain boundary slip when
additives are pesent. The evidence, however, is not conclusive.
Further, Chang suggested a new mechanism of grain boundary relaxation

based on creep and anelastic studies: a stress-induced formation, migration and annihilation of vacancies. At grain boundaries under tensile stress, vacancies (above equilibrium concentration) are formed. The activation energy of the process is the sum of that for formation and migration of a vacancy, which is the activation energy for self diffusion. When solute atoms are present, the activation energies for formation and migration of a vacancy near the solute atoms are markedly lowered. A new relaxation process involving the solute atom arises, presumable caused by stress induced formation, migration and annihilation of vacancy-solute aggregates near grain boundary. Further studies are required to verify the mechanism.

Further observations concerning the elastic behavior of poycrystalline materials have been made by Wachtman[33] and Ault[34]. Again, in these investigations, no special comments were made concerning the microstructure of test specimens. Wachtman and Ault find non-linear decreases in elasticity of polycrystalline alumina from 600° to 900^oC. Crandall also worked with Al_2O_3 + 1 wt.% SiO_2. According to Crandall et. al., X-ray examinations of all such samples revealed that mullite was formed with each addition of silica. One percent addition of silica produced 3% mullite; 3% silica addition produced 10% mullite; and 5% silica addition produced 17% mullite by weight. They found an internal friction peak around 700^oC attributing it to the same phenomenon observed by Chang in Al_2O_3 with additions of Cr_2O_3 or La_2O_3. Turnbough and Norton[35] found glassy phase in Wachtman[31] and Chang[30] alumina samples and also in Chang's[30] Al_2O_3-Cr_2O_3 samples. They observed two relaxation mechanisms in alumina. Type I, a lower temperature relaxation, associated with a

peak, is impurity dependent. According to them a peak exists when the relaxation phenomena involves a back stress. On the other hand, Type II relaxation rises continuously without exhibiting a maximum and occurs at higher temperatures. According to them, it appears to stem from the intrinsic properties of grain boundaries as it was absent in single crystal Al_2O_3 even at temperatures where single crystal Al_2O deformed visibly and was present in those polycrystalline specimens which contained no viscous phase. It was interpreted as arising from diffusion controlled grain boundary motion in Al_2O_3.

An activation energy of 35 Kcal/mole was found to be associated with Type I relaxation in one of their Al_2O_3 sample which is within the range for viscous flow in silicate glasses. Chemical analysis of their alumina indicated the presence of impurites such as silica and alkali oxides. Impurity additions such as Cr_2O_3 and SiO_2 which should go into solid solution or form crystalline nonviscous phases respectively with the alumina at 1675°C for 3 hours do not appreciable alter Type II damping from that of pure alumina. According to them a small Type I peak in Al_2O_3 + 1 wt.% Cr_2O_3 is due to apparatus irregularities. It is to be noted that a viscous phase at grain boundaries is not just the result of impurities alone. In Al_2O_3-SiO_2 system, kinetic inaccessibility of formation of mullite makes metastability,[36-42] Fig. 6-1, realizable under normal experimental conditions. A sintering study[43] of mixed powders of alumina and silica show that formation of a viscous phase is a precursor to formation of mullite.

Alumina with 1.5 wt.% silica sample was hot pressed starting from appropriately mixed powders of alumina and quartz. The sample was hot pressed at 1550°C for one hour.

The initial drop in elastic modulus due to thermal vibrational energy is the same for commercial Al_2O_3 and Al_2O_3 + 1.5 wt.% SiO_2 and can be explained by low solid solubility of SiO_2 in Al_2O_3. In this temperature range grain boundaries are not mobile. Corresponding Q^{-1} vs temperature for Al_2O_3 + 1.5 wt.% SiO_2 is shown in Fig. 6-10. The glass grain boundaries relax around 730°C which is close to glass transition temperature of alumino silicate glasses. The activation energy was found to be 45 $\pm$ 5 Kcal/mole. The activation energy matches well with literature values of activation energies obtained from bulk viscosity measurements.[44-45]

The drop in elastic modulus due to grain boundary sliding for 71.8 wt.% alumina and 28.2 wt.% SiO_2 sample having a continuous film of glassy phase at grain boundaries is shown in Fig. 6-13 and Table 6-6. Internal friction versus temperature plot is shown in Fig. 6-15 and Table 6-8. A corresponding drop in elastic modulus for 75 wt.% alumina and 25 wt.% silica sample is shown in Fig. 6-14 and Table 6-7. Internal friction versus temperature plot is shown in Fig. 7-1 and Table 7-1.

Thus dynamic elastic moduli and internal friction can be measured using electromagnetic transducers with special modification.

CHAPTER 7

RESULTS AND DISCUSSION

7.1. The Damping Spectra

The damping spectra for mullite (75 wt.% Al_2O_3) having single phase microstructure is shown in Fig. 7-1 and Table 7-1. Corresponding spectra for sample with glassy phase at grain boundaries (mullite 71.8 wt.% Al_2O_3) is shown in Fig. 6-15 and Table 6-6.

7.2. Comparison of Results with Theory

In order to determine if the mechanisms proposed for different micro-structures are valid, experiments were conducted for the case of single phase microstructure and for the case of glassy phase at grain boundaries. The relaxation time τ for comparison with Eq. (5-1) for single phase microstructure and also for glassy phase microstructure was calculated from the condition $\omega\tau = 1$ where $\omega = 2\pi f$, is angular frequency of oscillation at the damping maximum. The normalization of the relaxation time for the variables of the experiment (excepting temperature) leads to Eq. (5.1) for the case of single phase microstructure and also for the case of microstructure with glassy phase at grain boundaries. Thus the theoretically calculated values are from the right hand side of the Eq. (5.1) for the two microstructures respectively. These are compared against experimental measurements of the left hand side of Eq. (5.1) corresponding to the two microstructures.

Table 7-1. Data on mullite (75 wt.% Al_2O_3)

$T{}^{o}C$	f_r (c/s)	Δf_r (c/s)	$Q^{-1}*10^3$	Q^{-1}_{Norm}
100	3543	4.44	2.302	
506	3472	4.57	2.416	
801	3420	4.68	2.511	0.119
817	3419	5.13	2.753	0.229
829	3410	6.28	3.383	0.370
852	3407	6.96	3.748	0.514
881	3405	9.23	4.975	0.950
897 (T_p)	3384	9.13	4.951	0.995
905	3383	7.00	3.801	
917	3374	4.52	2.461	
926	3373	4.43	2.461	0.817
941	3370	4.57	2.462	0.641
956	3364	4.57	2.463	0.400
988	3357	4.63	2.500	0.231
1018	3355	4.56	2.493	0.08
1035	3348	4.836	2.652	
1054	3345	5.20	2.854	
1097	3341	6.61	3.635	
1139	3327	9.50	5.178	
1172	3320	15.10	8.249	
1181	3319	19.17	10.475	

Normalized relaxation times for various tests are plotted logarith-
mically against reciprocal absolute temperature for single phase micro-
structure in Fig. 7-2 and Table 7-2 where it may be noted that the acti-
vation energy of 160 ± 20 Kcal/mole was obtained from the slope which
matches well with literature values.[1-2] Corresponding graphs of nor-
malized relaxation times for various tests are plotted logarithmically
against reciprocal absolute temperature for microstructures having con-
tinuous glassy film at grain boudaries in Fig. 7-3 and Table 7-3, where
it may be noted that activation energy of 95 ± 5 Kcal/mole was obtained
from the slope which matches well with literature values.[3-4]

Table 7-2. Internal friction data for sample with single phase micro-
structure ($\theta = 30°$; $\kappa = 1.38$ corresponding to a/1 = 0.37,
Q = 160 ± 20 Kcal/mole)

T (K)	f_r(c/s)	$*10^5$s	$(\eta/\delta)_i *10^{-13}$ kg/m^2·s	ln(L.H.S.) (Eq. 5.1)	ln(R.H.S.) (Eq. 5.1)
1145	1,156	13.77	11.53	4.56	5.31
1176	7,213	2.21	1.85	2.73	3.48
1190	15,650	1.02	0.85	1.96	2.71

Table 7-3. Internal friction data for sample having continuous glassy phase at grain boundaries ($\theta = 30^\circ$; $\kappa = 1.42$ corresponding to $a/1 = 0.275$, $Q = 95 \pm 5$ Kcal/mole)

T(K)	f_r(c/s)	$*10^5$s	$(\eta/\delta)_i *10^{-13}$ kg/m$^2\cdot$s	ln(L.H.S.) (Eq. 5.2)	ln(R.H.S.) (Eq. 5.2)
986	2,109	7.55	5.24	4.18	4.60
1014	7,993	1.99	1.38	2.85	3.27
1026	14,166	1.12	0.78	2.27	2.70

The discrepancy between experimental data and theoretical prediction is partly due to using viscosity/unit thickness values for dense samples. Viscosity as well as effective grain boundary thickness might be different for cavitated and fully dense samples for the two microstructures under consideration. Further, not all grain boundaries relax at the same time and equiaxed grains are assumed in the analysis.

We interpret this to mean that grain boundary damping peaks observed in case of single phase microstructure and microstructure with glassy phase at grain boundaries result from grain boundary sliding accommodated by elastic deformation of the grains. The rate of sliding is controlled by grain boundary diffusion and cavities only play a small role in the accommodation process for the case of single phase microstructure as obvious from Fig. 2-3 and only ~20°C lowering in temperature due to the presence of cavities. Correspondingly the rate of sliding is controlled by viscous deformation (with no diffusion involved) and cavities also play only a minor role in the accommodation process for the case in which glassy phase is present at grain boundaries as obvious from Fig. 2-3 and

only $\sim 30^{o}$C lowering in temperature due to presence of cavities. The activation energy did not change due to the presence of cavities which further indicates the small role played by cavities in the deformation process.

CHAPTER 8

HIGH TEMPERATURE BACKGROUND

8.1. Introduction

Zener[1] recognized, early, that thermal or atomic diffusion between grain boundaries, or near grain boundaries could contribute to damping. This results because thermoelastic differences between adjacent grains cause local stresses or strains near boundaries. These provide driving forces for redistribution of heat or solute atoms to new equilibrium configuration under load. However, because there are equilibrium end states, thermal or solute diffusion to grain boundaries will cause damping with distinct peaks; although as Zener[1] showed, they do not satisfy a simple Debye frequency relation. These losses are generally small compared to the sliding losses and predominant at different frequencies. Several other damping peaks caused by various solute diffusion mechanisms have been extensively investigated by De Batiste,[2] Nowick and Berry,[3] but are generally not unique to polycrystalline materials and will not be considered here.

Later it was recognized by Friedel[4] and Escaig[5] that defect diffusion, that is, cyclic Nabarro-Herring creep, can also cause damping. For diffusion to and from boundaries there is no equilibrium end state and so background loss will increase without a limit at high temperature or low frequency. Diffusion can similarly cause cyclic dislocation climb; in principle, this can also increase without limit at low frequency, although at low stresses climb may be limited by the dislocation line tension giving a stress dependent limiting strain. Glide dislocations of course, also cause damping, but any slip involved in the high

temperature polycrystalline background is likely directly related to the stress concentrations at grain boundaries in contrast to the lower temperature peaks found in both single crystals and polycrystals. Gifkins[6] and others have also suggested that diffusion at small ledges may be a limiting process in the sliding peak; however, depending upon the size of the steps, this process becomes indistinguishable from the background loss.

High temperature background has been analyzed here in terms of grain boundary diffusion in the transient case of non-uniform thickening of grain boundary.

8.2. Grain Boundary Sliding

When a remote stress σ_∞ is applied to a polycrystal, boundary sliding occurs with a relatively short relaxation time to generate stress singularities on adjacent boundaries (Fig. 8-1). The magnitude of singularities depends on the deformation properties of the material. For most polycrystalline ceramics, the grain can be assumed to respond in a linear viscous fashion. For this case, bounds on the singularity can be obtained from a two-dimensional solution with completely relaxed grain boundaries,[7]

$$\sigma \gtrsim 0.41\sigma_\infty \sqrt{d/x} = K_u/\sqrt{x} \qquad (8.1a)$$

where σ is the local stress, σ_∞ the remote stress, d the grain facet length and x the distance from the triple point; and from the solution for a single mode II penny crack[8]

$$\sigma \gtrsim 0.18\,\sigma_\infty \sqrt{d/x} = K_L/\sqrt{x} \qquad (8.1b)$$

These high local tensile stresses induce vacancy formation at boundary sources (to develop a vacancy supersaturation). The vacancies then diffuse to adjacent (compressively stressed) boundaries, and the stress singularity dissapears, as indicated in Fig. 8-1. The relaxed stress distribution can be estimated by assuming that the time-dependent stress distribution $\sigma(x,t)$ has the form at $t = 0$ suggested by Eq. (8.1) and Fig. 8-2, viz:

$$\sigma(x,0) = \begin{cases} K/\sqrt{x} & x > 0 \\ \\ -K/\sqrt{-x} & x < 0 \end{cases} \qquad (8.2)$$

If $\delta = \delta(x,t)$ is the effective "thickening" of the grain boundary (due to the addition of matter to the crystals on each side), and J is the number of atoms diffusing along the grain boundary per unit time, per unit thickness into the plane of the diagram, mass conservation requires that

$$\Omega \partial J/\partial x + \partial \delta/\partial t = 0 \qquad (8.3)$$

Further, the linearized law of diffusion is[9,10]

$$\Omega J = - \frac{D_b \delta_b}{KT} \frac{\partial}{\partial x} (-\Omega \sigma) \qquad (8.4)$$

where the equation has been arranged to emphasize that $-\Omega \sigma$ is the chemical potential per atom. Here $D_b \delta_b$ is the grain boundary diffusion parameter. Hence,

$$\frac{D_b \delta_b \Omega}{KT} \frac{\delta^2 \sigma}{\partial x^2} + \frac{\partial \delta}{\partial t} = 0 \qquad (8.5)$$

A standard result of plane strain isotropic elasticity indicates that for a stress distribution

$$\sigma(x,t) = B(t)e^{-i\gamma x} \qquad (8.6)$$

where B contains the time dependence of the stress acting along the axis. The required distribution of the "thickening" displacement is twice the surface displacement in the corresponding problem of load application to a half space. Thus e.g., following Chuang[9] and Chuang et al.,[11]

$$\delta(x,t) = - (2(1-\nu)/G\gamma)/B(t)e^{i\gamma x} \qquad (8.7)$$

where G is the elastic shear modulus and   in Poissons ratio. If the express ions for   and   are to satisfy the diffusion equation (3), it is necessary that

$$B(t) = B_o \exp(-\alpha|\gamma|^3 t) \qquad (8.8)$$

where

$$= \frac{G\delta_b D_b \Omega}{2(1-\nu)kT}$$

Hence if the initial stress distribution of Fig. 8-2 is represented by

$$\sigma(x,0) = \int_{-\infty}^{\infty} B_o(\gamma)e^{i\gamma x} d\gamma \qquad (8.10)$$

the stress distribution at any time $t > 0$ is

$$\sigma(x,t) = \int_{-\infty}^{\infty} B_o(\gamma)\exp(-\alpha|\gamma|^3 t)e^{i\gamma x}d\gamma \qquad (8.11)$$

By Fourier inversion of Eq. (8.11) and a straight forward integration based on the form given earlier for $\sigma(x,0)$ gives the result

$$B_o(\gamma) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sigma(x,0)e^{-i\gamma x}dx \qquad (8.12a)$$

$$= \frac{K}{2\pi} \left[-\int_{0}^{\infty} x'^{-1/2}e^{i\gamma x'}dx' + \int_{0}^{\infty} x^{-1/2}e^{-i\gamma x}dx \right] \qquad (8.12b)$$

where $x' = -x$

$$= \begin{cases} -iK/2\sqrt{2\pi}\ |\gamma|^{1/2} & \gamma > 0 \\[2em] iK/2\ \sqrt{2\pi}|\gamma|^{1/2} & \gamma < 0 \end{cases} \qquad (8.12c)$$

where these results are inserted into the integral for $\sigma(x,t)$ (Eq. (8.11)) with $u^2 = \gamma x$ and $z = \alpha t/x^3$, the result is

$$\sigma(x,t) = \frac{K}{x^{1/2}} \cdot f(\alpha t/x^3) \qquad (8.13)$$

where

$$f(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-zu^6) \, \sin u^2 \, du \tag{8.14}$$

which is plotted in Fig. 8-3 and can be represented as

$f(z) \approx 0.24 \, \exp(-0.095z)$. In case of internal friction $K = K_0 \, \cos \omega t$,

then by standard superposition techniques

$$\sigma(x,t) = \int_{-\infty}^{t} \frac{dK(t')/dt'}{x^{1/2}} \, f\left(\frac{\alpha(t-t')}{x^3}\right) dt' \tag{8.15}$$

with $t'' = t-t'$, we get

$$\sigma(x,t) = -0.24\omega \int_{0}^{\infty} K_0 \, \frac{\sin(t-t'')}{x^{1/2}} \cdot \exp(-0.095\alpha t''/x^3) dt'' \tag{8.16}$$

with $q = \omega x^3/\alpha$ leads to

$$\sigma(x,t) = K_0 \left(\frac{\omega}{\alpha}\right)^{1/6} \left[\cos\omega t \, G(q) - \sin\omega t \, H(q)\right] \tag{8.17a}$$

where

$$G(q) = 0.24 \int_{0}^{\infty} q^{5/6} \cdot \sin qz \cdot \exp(-0.095z) dz \tag{8.17b}$$

$$= \frac{0.35 \, p^{11/6}}{1 + p^2} \tag{8.17c}$$

where $p \approx 10q$

and

$$H(q) = 0.24 \int_0^\infty q^{5/6} \cos qz \cdot \exp(-0.095z)dz \qquad (8.17d)$$

$$= \frac{0.35\, p^{5/6}}{1 + p^2} \qquad (8.17e)$$

The average stress is obtained from

$$\sigma_{av} = \frac{2}{d} \int_0^{d/2} \sigma(x,t)dx \qquad (8.18a)$$

and is

$$\sigma_{av} = 2\,\frac{K_o}{d}\left(\frac{\omega}{\alpha}\right)^{1/6}\left[\cos\omega t\int_0^{d/2} G\!\left(\frac{\omega}{\alpha}\,x^3\right)dx - \sin\omega t\int_0^{d/2} H\!\left(\frac{\omega}{\alpha}\,x^3\right)dx\right] \qquad (8.18b)$$

and internal friction Q^{-1}:

$$Q^{-1} = \frac{\displaystyle\int_0^{d/2} H\left(\frac{\omega}{\alpha}\,x^3\right)dx}{\displaystyle\int_0^{d/2} G\left(\frac{\omega}{\alpha}\,x^3\right)dx} \qquad (8.19a)$$

$$= \frac{\displaystyle\int_0^{p^*} \frac{p^{1/6}}{1+p^2}\, dp}{\displaystyle\int_0^{p^*} \frac{p^{7/6}}{1+p^2}\, dp} \qquad\qquad (8.19b)$$

where $p^* = \frac{5}{4}\frac{\omega}{\alpha} d^3$

(a) For $p^* < 1$, we get from Eq (8.19b)

$$Q^{-1} \approx \frac{13}{7p^*} \qquad\qquad (8.20a)$$

which is the steady state result

(b) For $p^* > 1$, the integral in numerator of Eq. (8.19b) converges to
~1.4 and denominator to $6(p^*)^{-1/6}$
Thus

$$Q^{-1} \approx 0.24(p^*)^{-1/6} \qquad\qquad (8.20b)$$

the transition from case (a) to (b) excess $p^* \approx 10$

The results are plotted in Fig. 8-4 where contribution to high tem-
perature background from diffusion accommodated grain boundary sliding
(Eq. (8.20b)) and from diffusion at grain corners[12] is shown along with
the total contribution to high temperature background internal friction
which results from Eqs. (8.20a,b) and Ref. 12. Data for Al_2O_3 (Ref. 13)
is also shown which matches well with the theory. The slight discrepancy

is due to grain size distribution and error in value of pre-exponential factor in diffusion data.[14].

Normalized stress distribution is shown in Fig. 8-5 (Appendix A) which shows that $x = 2.5(\alpha t)^{1/3}$ is a measure of the distance from the grain junction over which the stress concentration is seriously mitigated by diffusion. It is thus seen that the dimensionless parameter $(5(1-\nu^2) \ d^3 KT/E\Omega\delta_b D_b)$ is very suitable in representing data and future experimental data should be represented using this parameter.

CHAPTER 9

SUMMARY AND CONCLUSIONS

Grain boundary damping peaks in mullite (75 wt.% alumina) and a microstructure with 71.8 wt.% alumina and 28.2 wt.% SiO_2 with pre-existing cavities at grain boundaries were measured. The peaks were attributed to grain boundary sliding with elastic accommodation. It was thus concluded that:

1. Presence of pre-existing cavities had only a small contribution to the total grain boundary sliding.

2. The relaxation time for sliding varies with cavity size, cavity spacing and with grain size in accordance with models developed for the two microstructures.

3. The activation energy of the relaxation is in agreement with that for boundary diffusion in case of mullite with single phase microstructure.

4. The activation energy of the relaxation is in agreement with that of viscous flow in case of microstructure with a glassy phase at the grain boundaries with cavities behaving as shear cracks under grain boundary sliding.

5. The transient case for high temperature background was solved and it was well represented by a dimensionless parameter which was a function of frequency, grain size, elastic modulus and grain boundary diffusivity.

It is further concluded that internal friction measurements provide a useful method for measuring rates of grain boundary sliding with elastic accommodation.

APPENDIX A

RELAXED STRESS DISTRIBUTION

When Eq. (8.12c) is inserted in Eq. (8.11) and $\gamma = v^2/(\alpha t)^{1/3}$ is substituted, the result is

$$\sigma(x,t) = \frac{K}{(\alpha t)^{1/6}} \cdot H\left[\frac{x}{(\alpha t)^{1/3}}\right] \qquad (H.1)$$

where

$$H(Y) = \sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} \exp(-v^6) \cdot \sin(v^2 \cdot Y)dv \qquad (H.2)$$

where

$$Y = x/(\alpha t)^{1/3} \qquad (H.3)$$

A plot of normalized stress distribution is shown in Fig. 8-5, which depicts a maximum at $x = 2.5(\alpha t)^{1/3}$, which is a measure of the distance from the grain junction over which the stress concentration is seriously mitigated by diffusion.

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FIGURE CAPTIONS

Fig. 2-1.   The variations of stress intensity factor with crack length

and angle for a kinked crack subject to in-plane shear and

small closure tractions.

Fig. 2-2.   Variation of ratio of elastic displacement due triple point

cavities to mode II shear displacement as a function of cavity

size and angle.

Fig. 6-1.   The extensions of the SiO_2 and Al_2O_3 liquid to form the meta-

stable phase diagram without mullite superimposed on the

SiO_2-Al_2O_3 equilibrium phase diagram.

Fig. 6-2.   Transmission electron micrograph of mullite (75 wt.% Al_2O_3)

with equilibrium dihedral angles.

Fig. 6-3.   Cutaway view of hot pressing assembly. A-Pyrolytic graphite

spacers, B-water cooled steel ram for pressure application

(at top), C-graphite plunger, D-graphite die, E-powder charge,

F-thermocouple in protection tube (G), H-furnace can, I-furnace

lid lined with insulating felt, J-molybdenum mesh furnace

element, K-connections to power leads.

Fig. 6-4.   Scanning Electron Micrographs of Mullite (&7 wt.% Al_2O_3)

with cavities at grain boundaries.

Fig. 6-5.   Electron micrograph of mullite (71.8 wt.% Al_2O_3).

(a) Transmitter electron micrograph showing acute dihedral

angle and glassy phase. (b) Scanning electron micrograph

showing cavities at grain boundaries.

Fig. 6-6.   Block diagram used for apparatus used for bar resonance.

Fig. 6-7.   The resonant vibrations in a rectangular bar.

Fig. 2-1

XBL 806-10227

Fig. 2-2

XBL 809-11787

XBL 809-11685

Fig. 6-1

XBB 806-7166

Fig. 6-2

XBL 809-11689

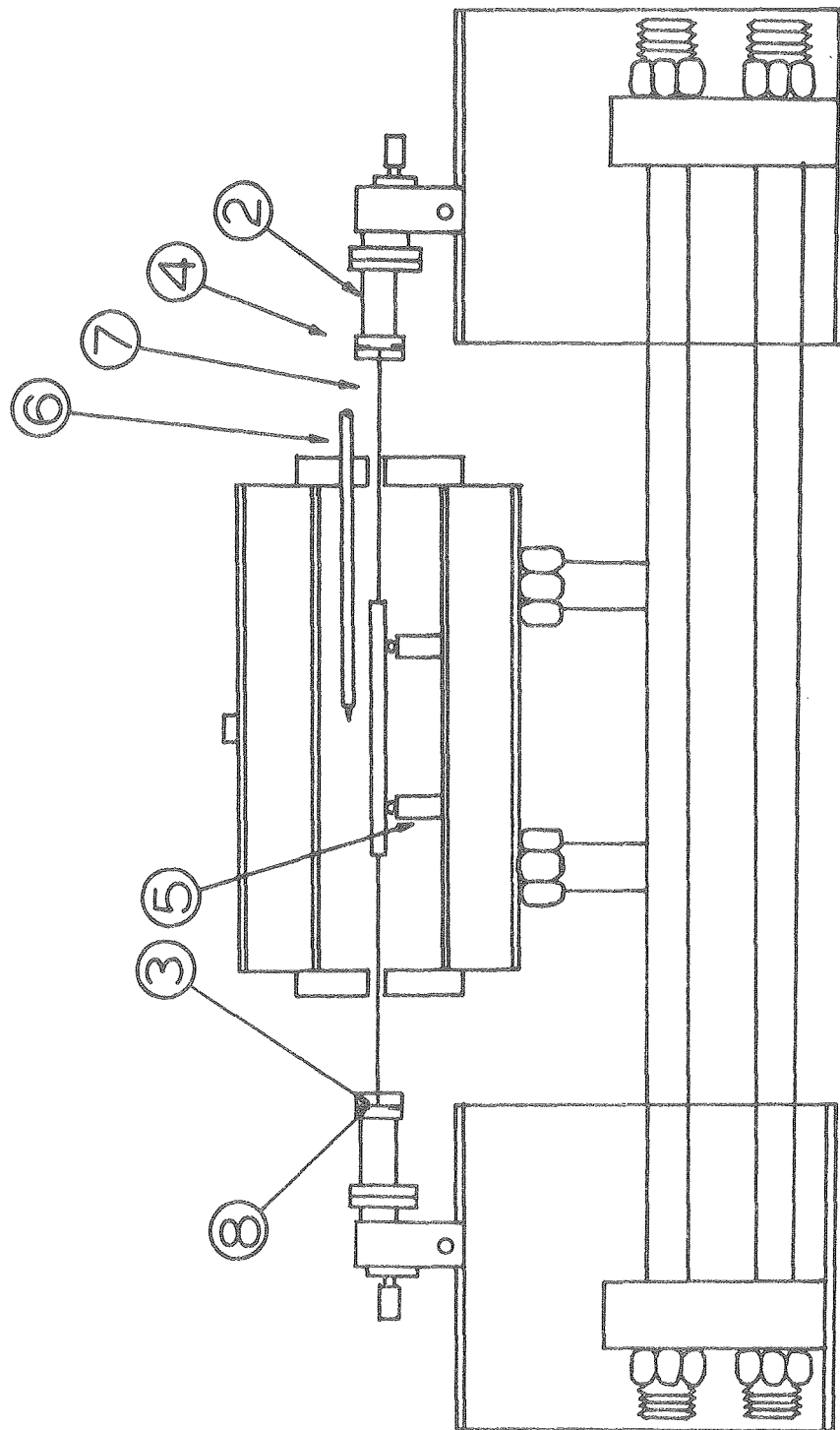Fig. 6-3
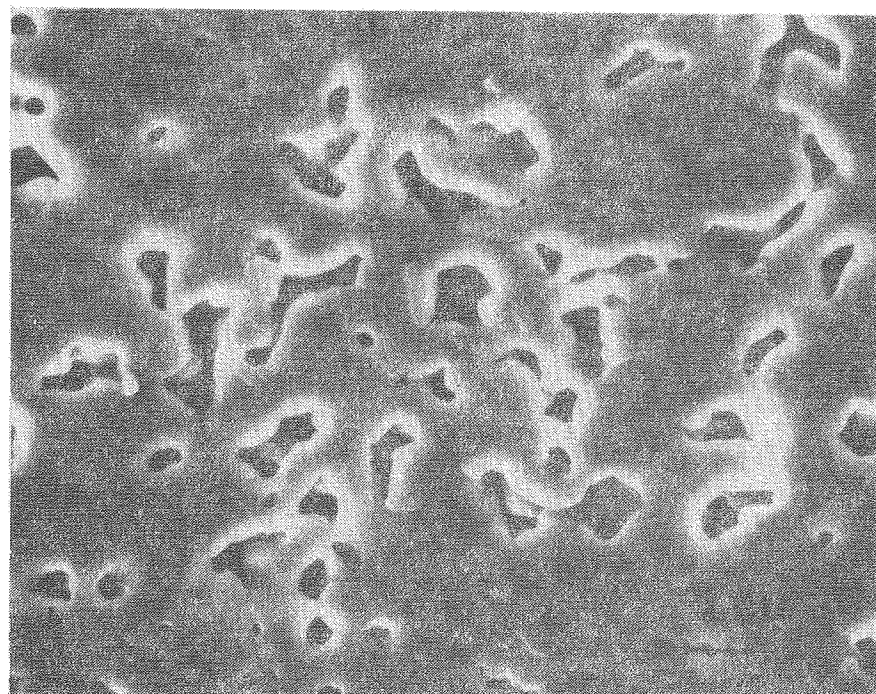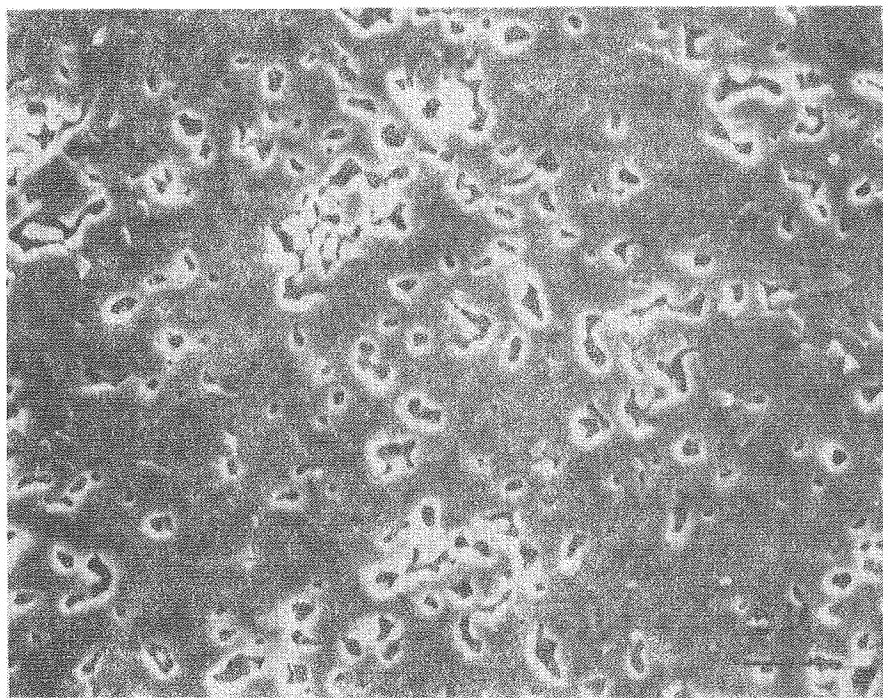
XBB 807-8233

Fig. 6-4

XBB 809-11041

Fig. 6-5

COUNTER

VARIABLE
FREQUENCY
OSCILLATOR

OSCILLOSCOPE

VOLTMETER
OR
AMMETER

POWER
AMPLIFIER

WIDE BAND
AMPLIFIER

FEED BACK
AMPLIFIER

TRANSMITTING
TRANSDUCER

RECEIVING
TRANSDUCER
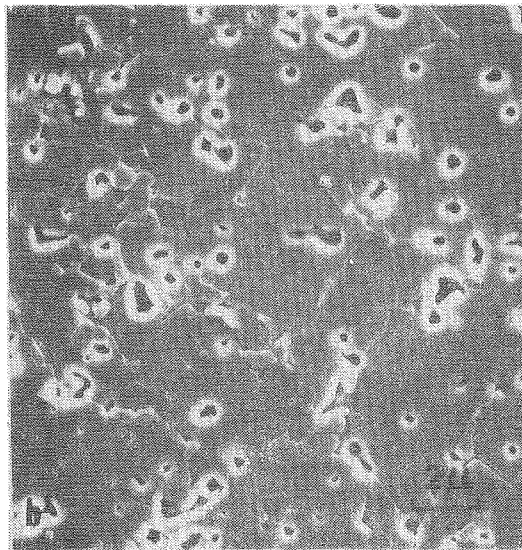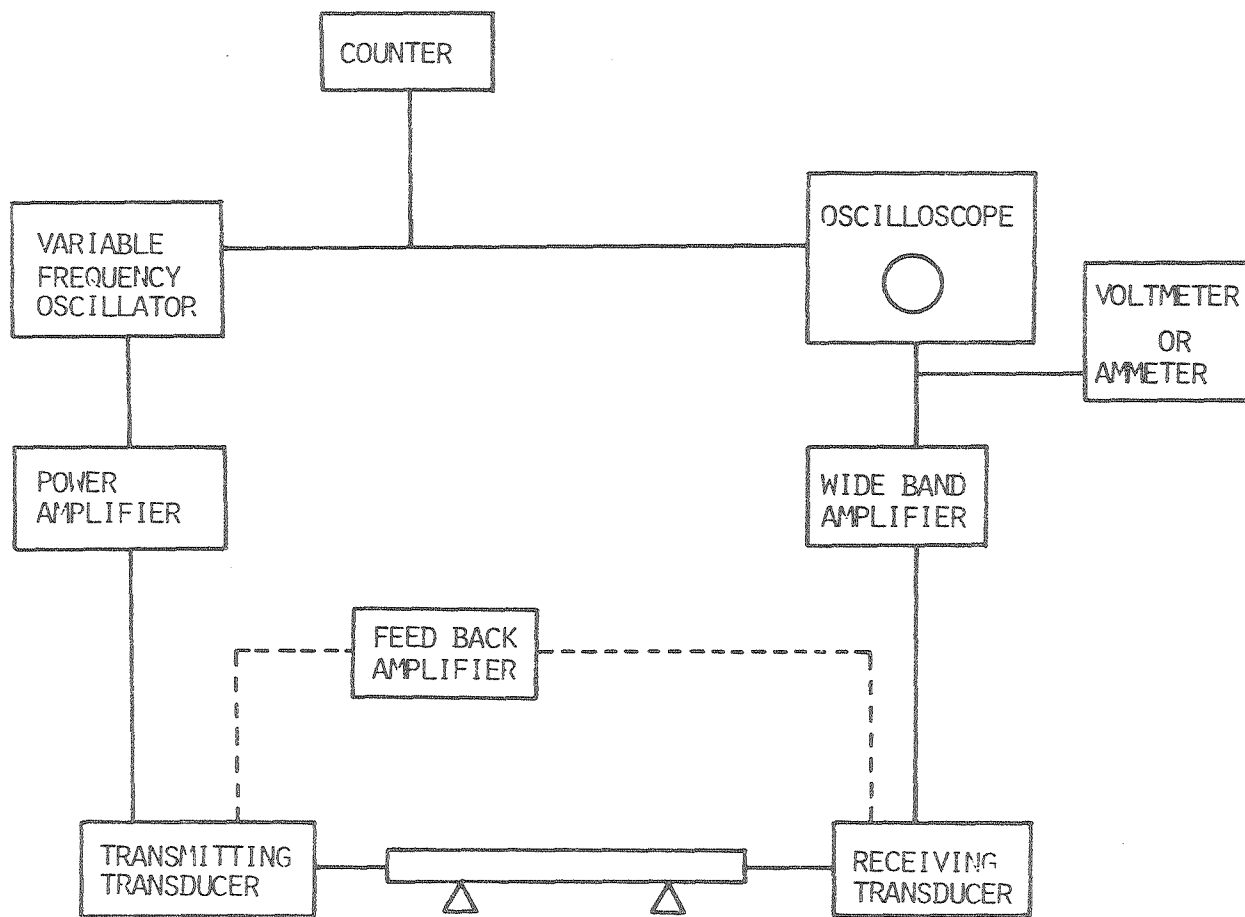
XBL 806-10228

Fig. 6-6
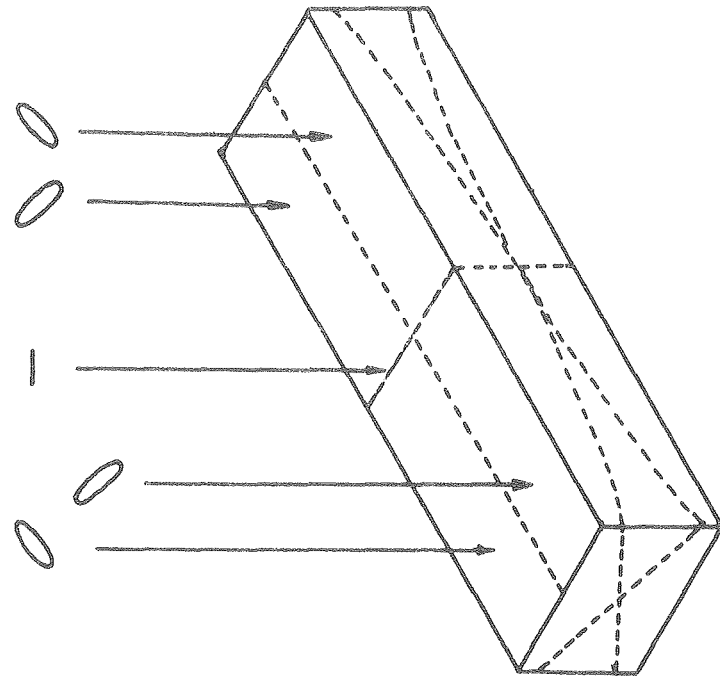
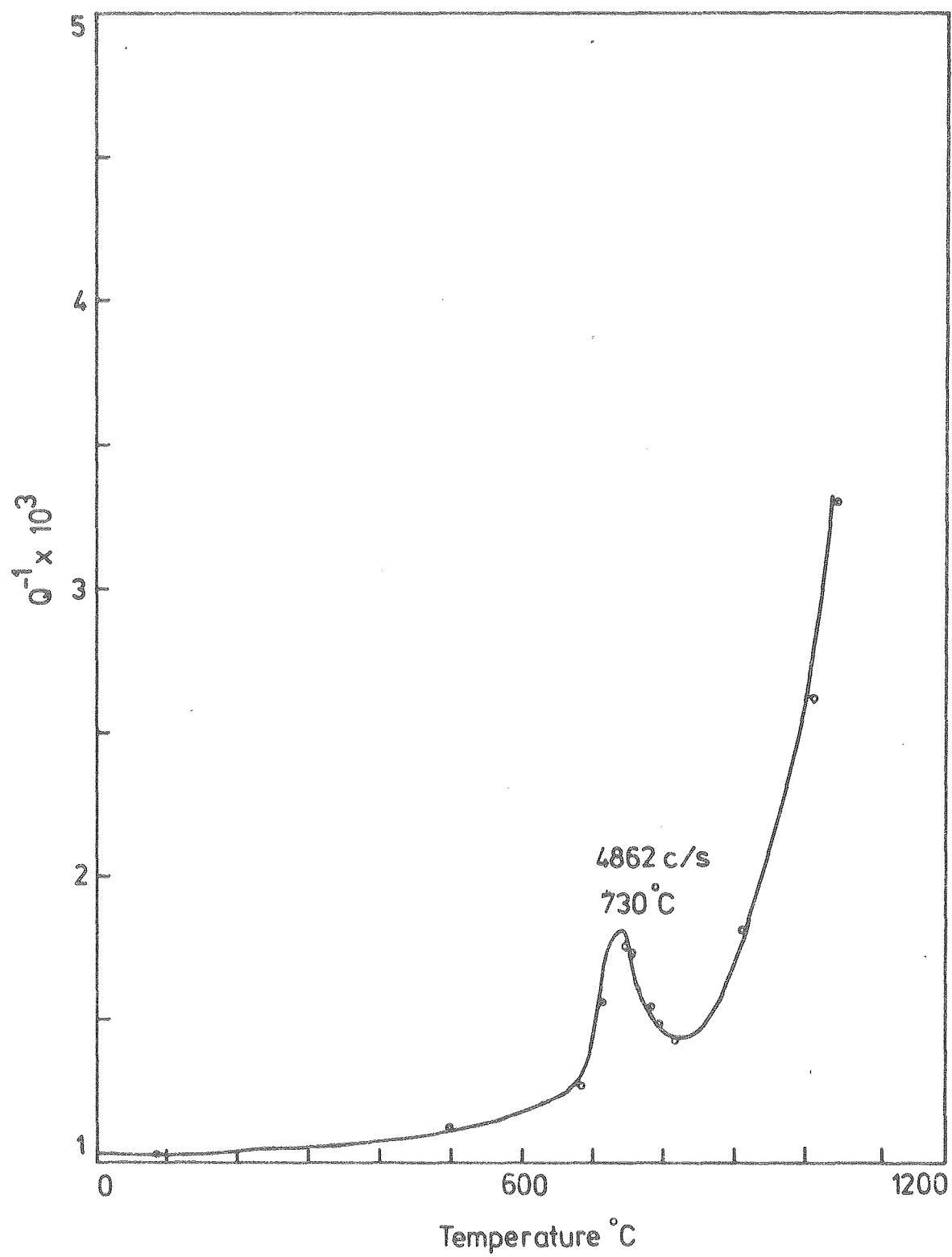(a) Flexural vibration
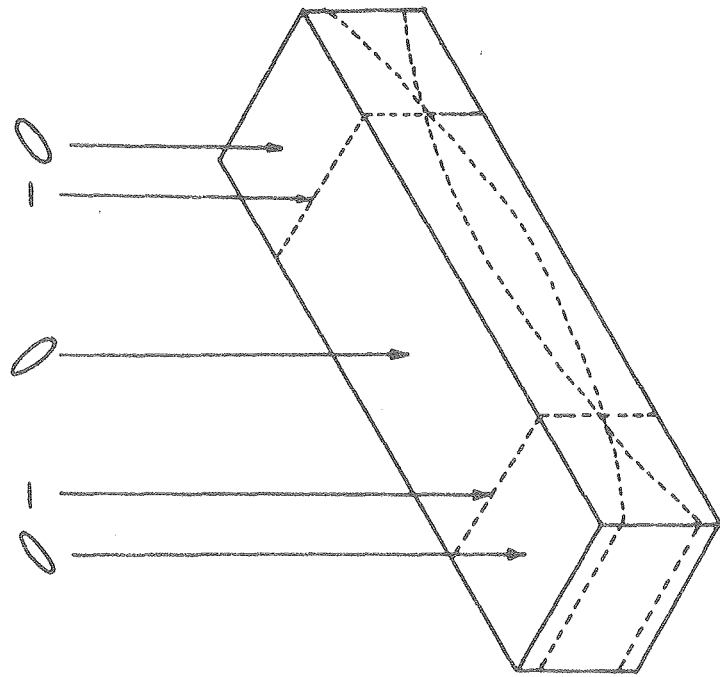
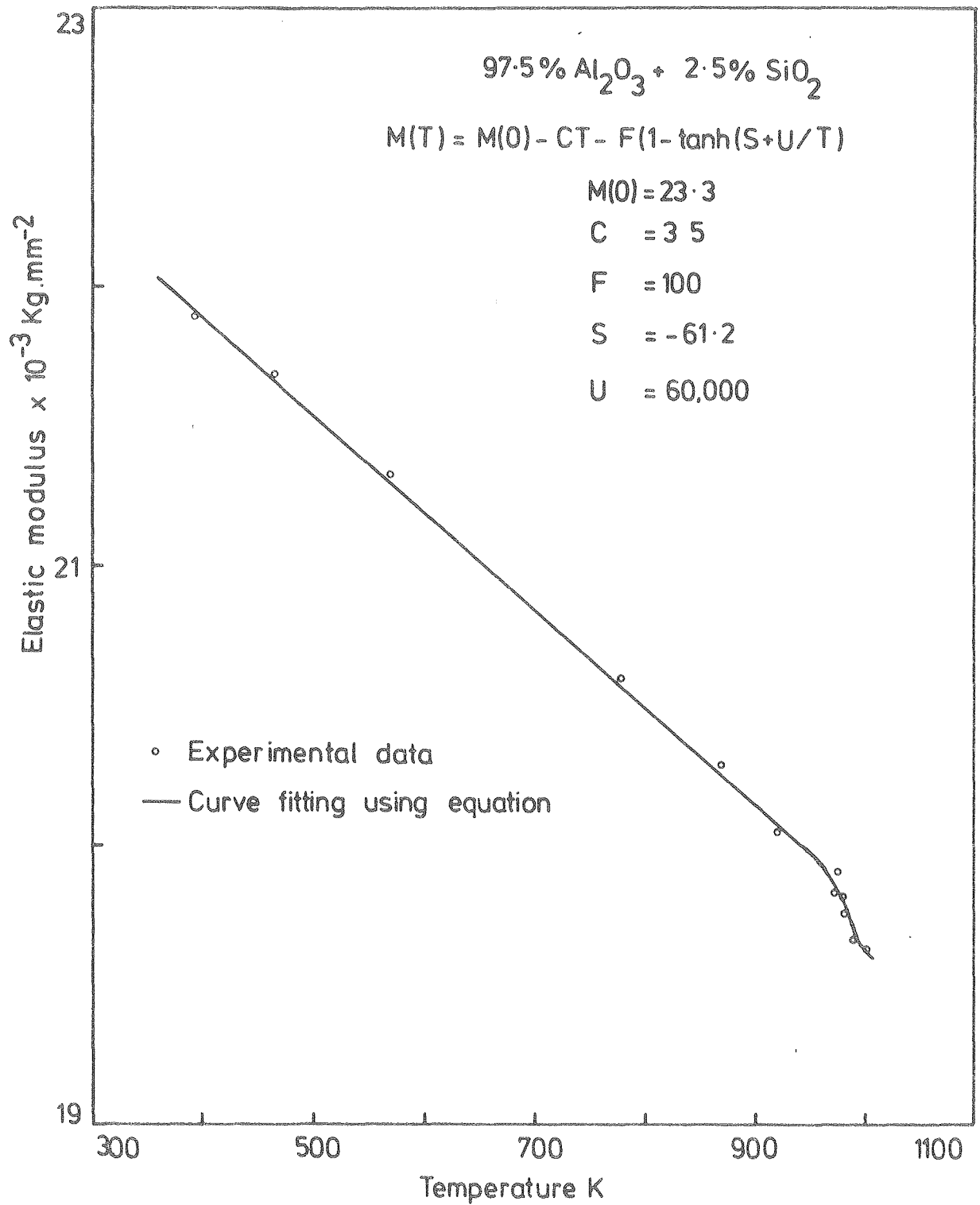(b) Torsional vibration

Fig. 6—7

XBL 809-11688

84

XBL 806-10229

Fig. 6-8

Fig. 6-9

Fig. 6-10

XBL 809-11687

$$M(T) = M(0) - CT - F(1 - \tanh(S + U/T))$$

97·5% Al_2O_3 + 2·5% SiO_2

$M(0) = 23 \cdot 3$

$C = 3\ 5$

$F = 100$

$S = -61 \cdot 2$

$U = 60,000$

○ Experimental data

— Curve fitting using equation
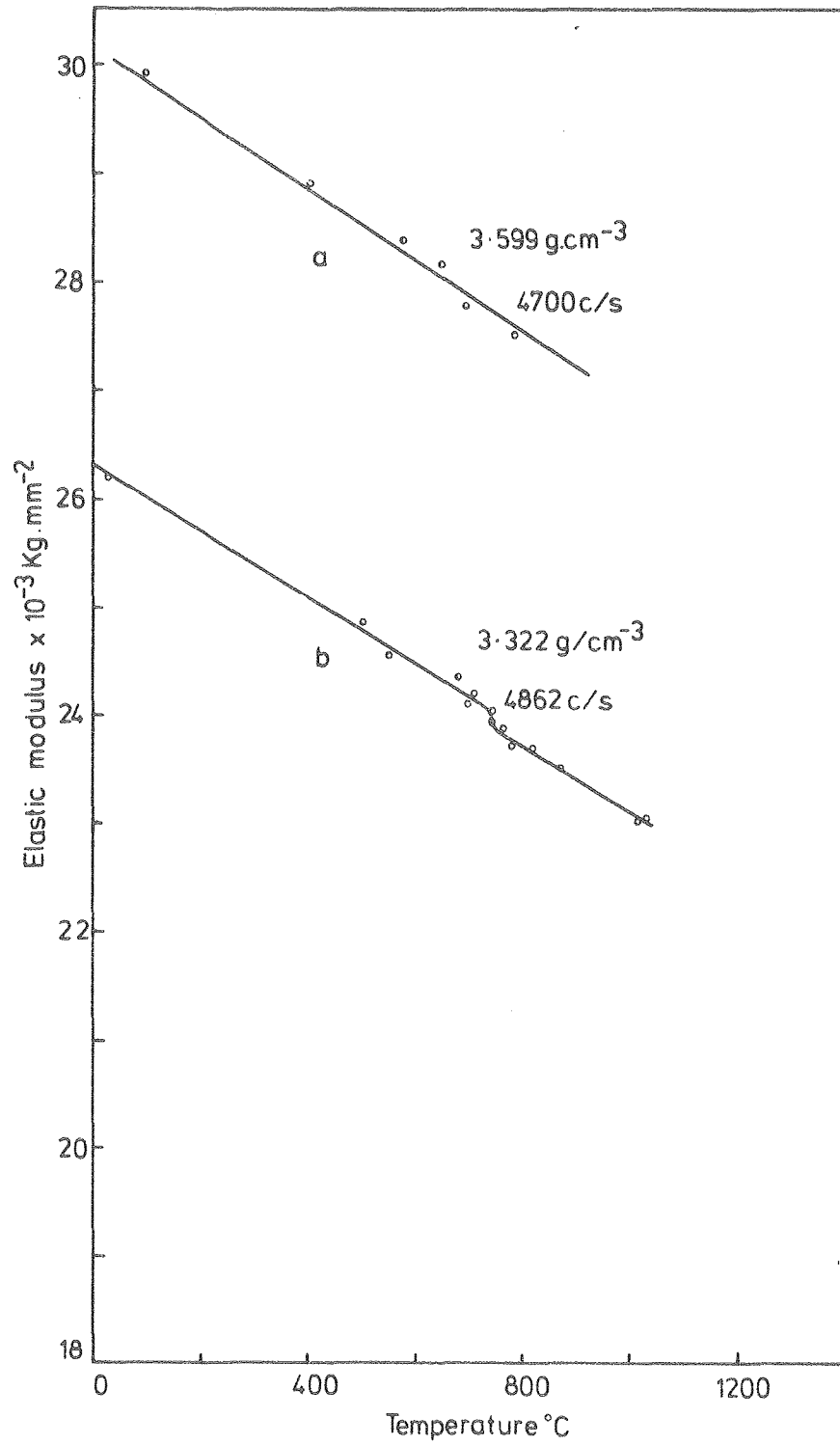
XBL 809-11691

Fig. 6-11

88
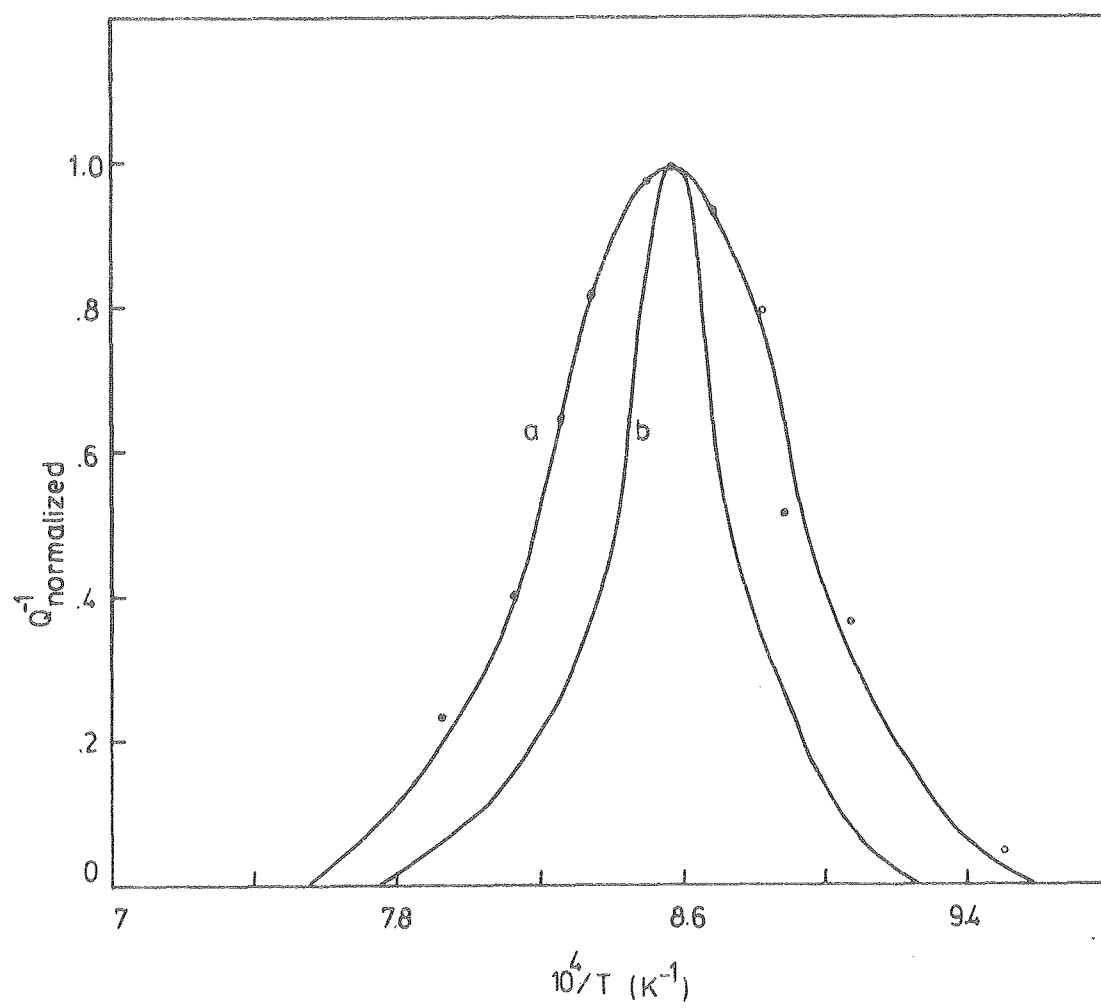
Fig. 6-12

XBL 809-11690
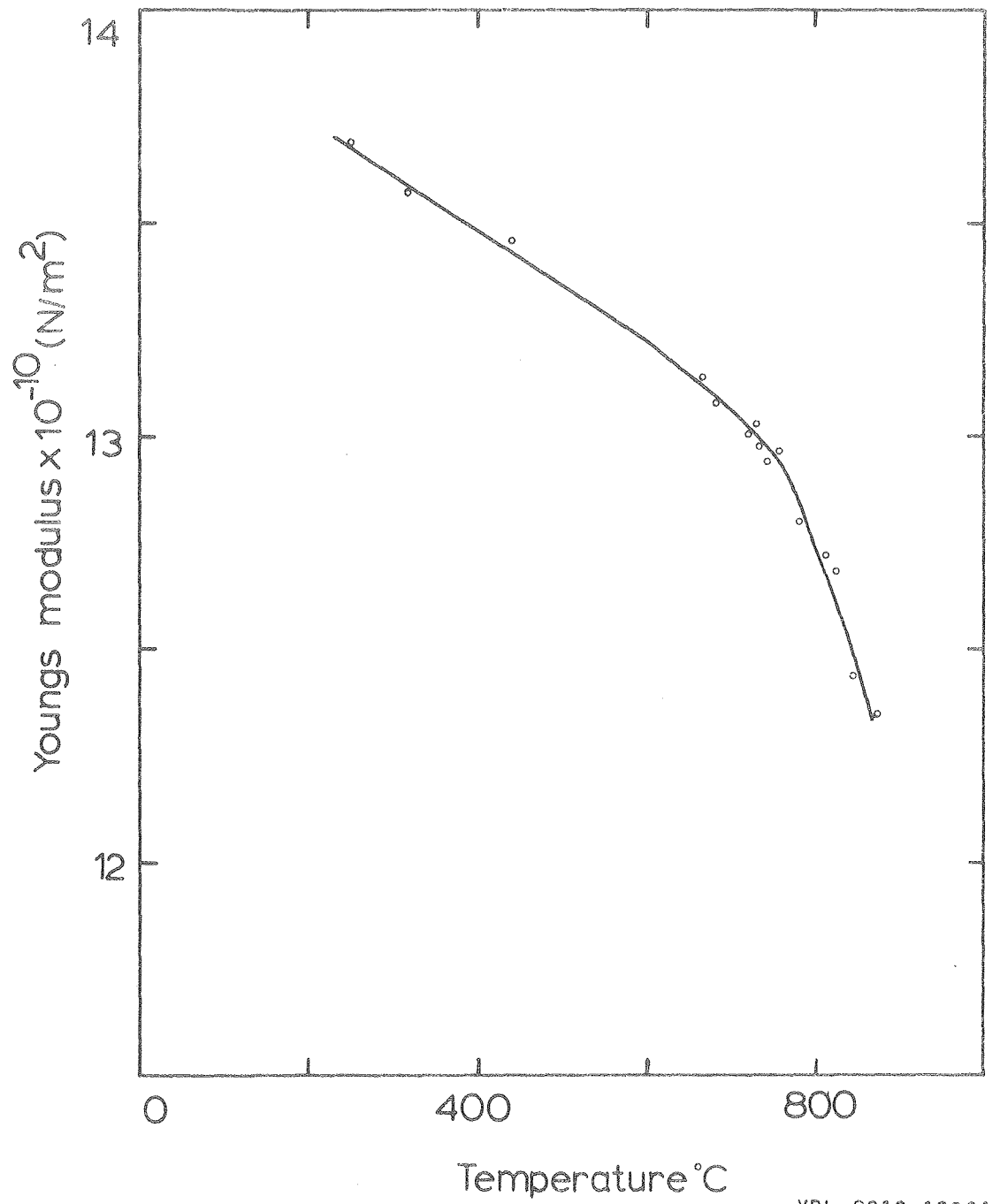
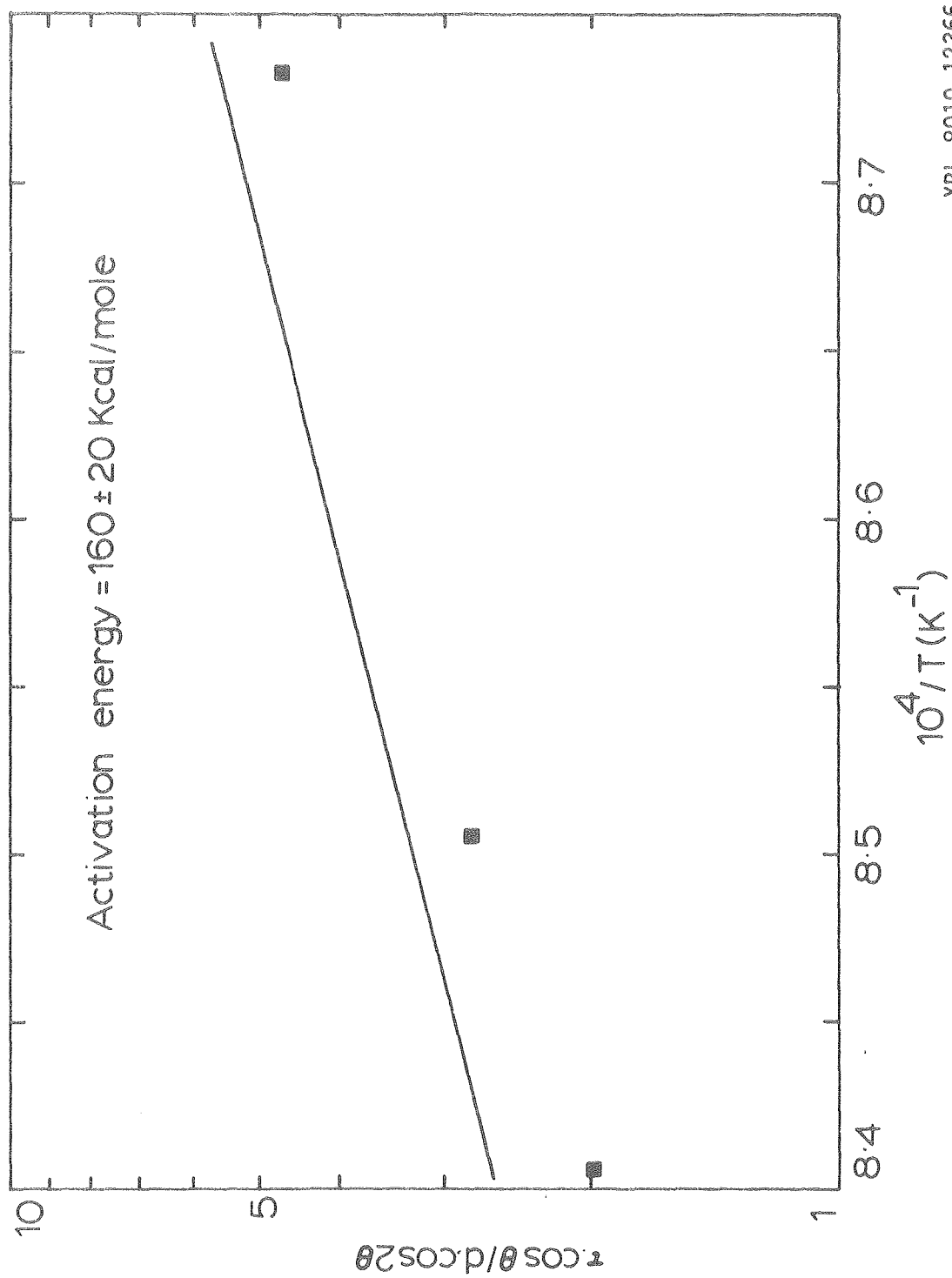Fig. 6-13

XBL 8010-12364
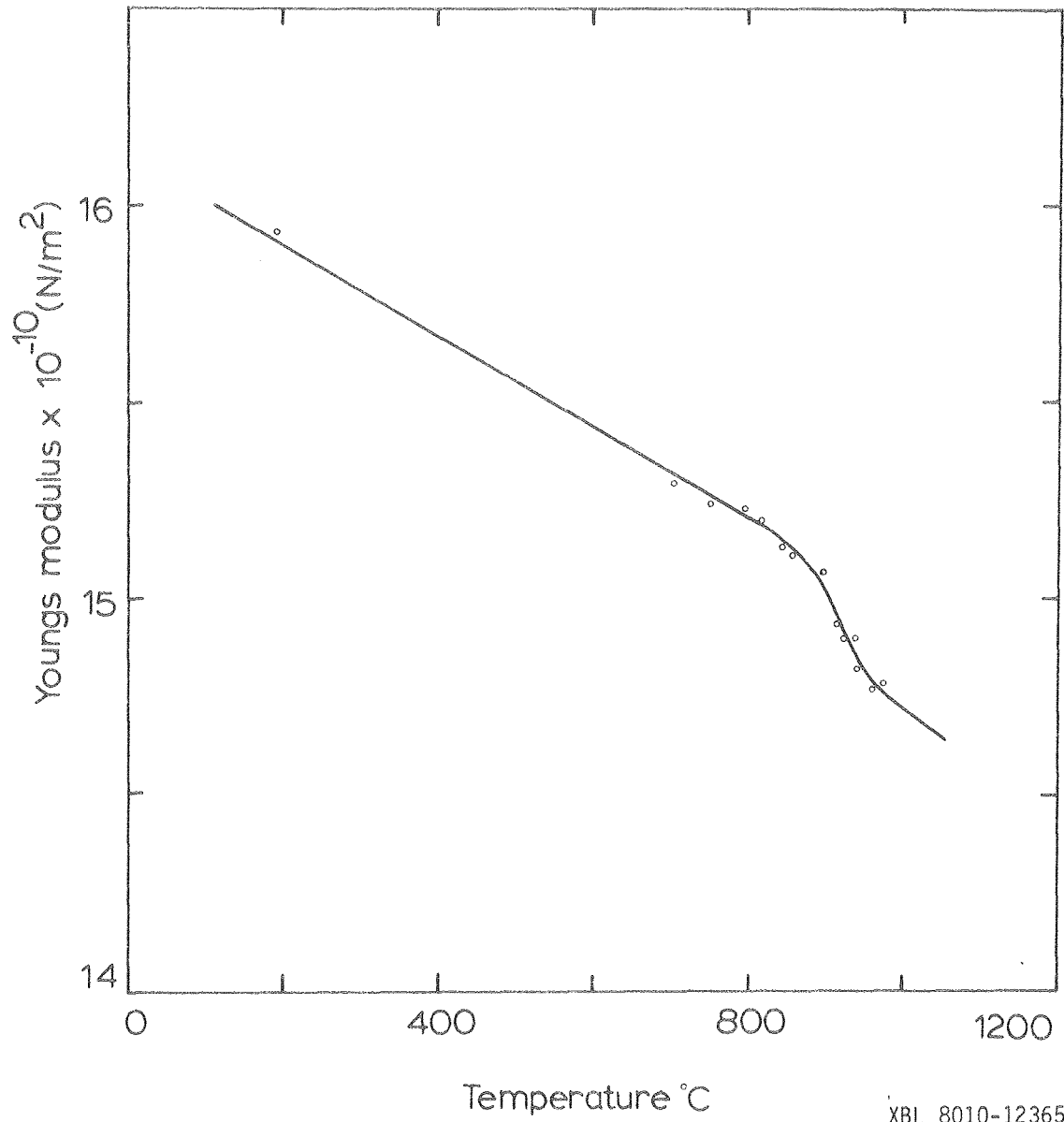
Fig. 6-14

XBL 8010-12365
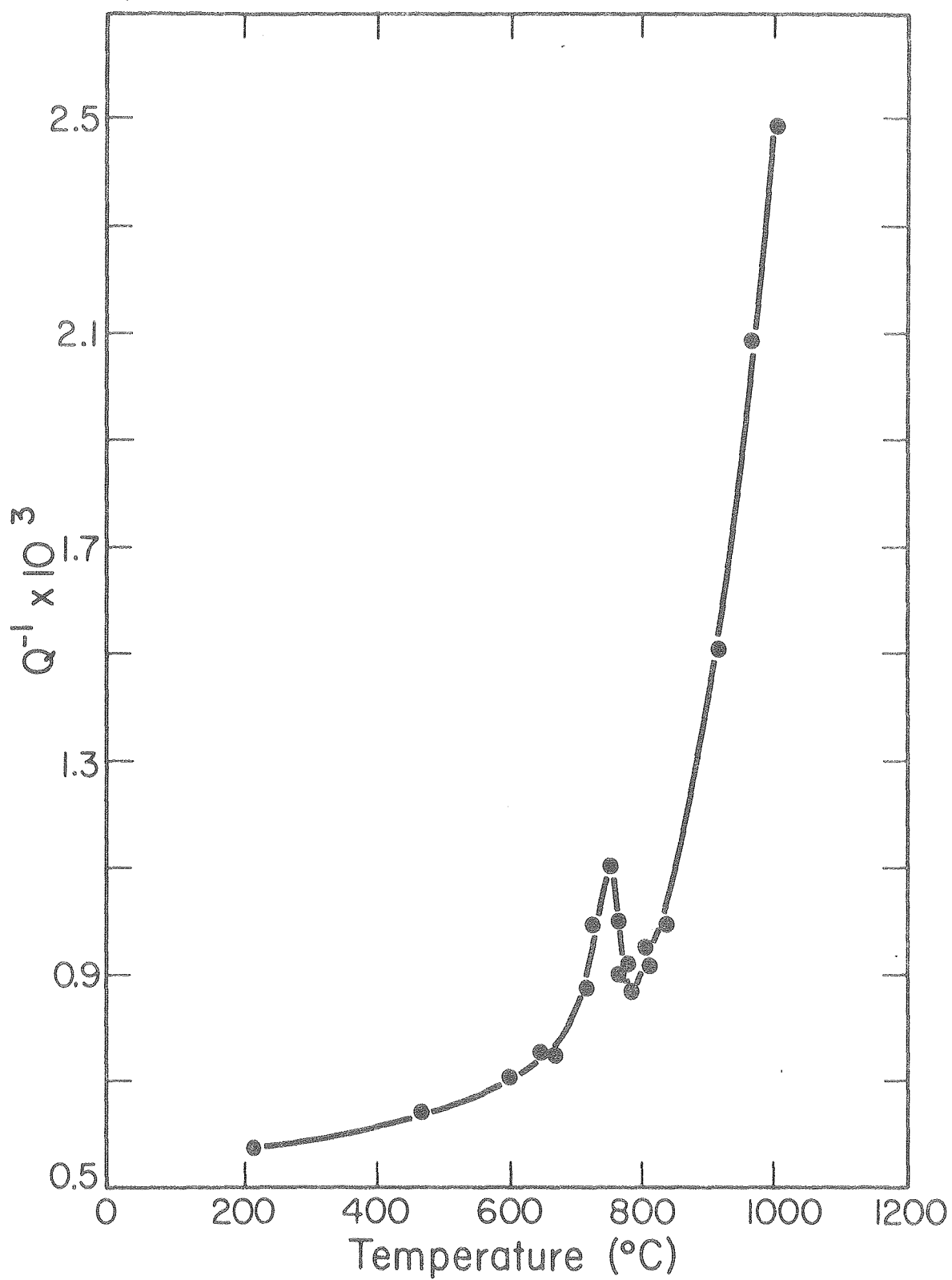
Fig. 6-15
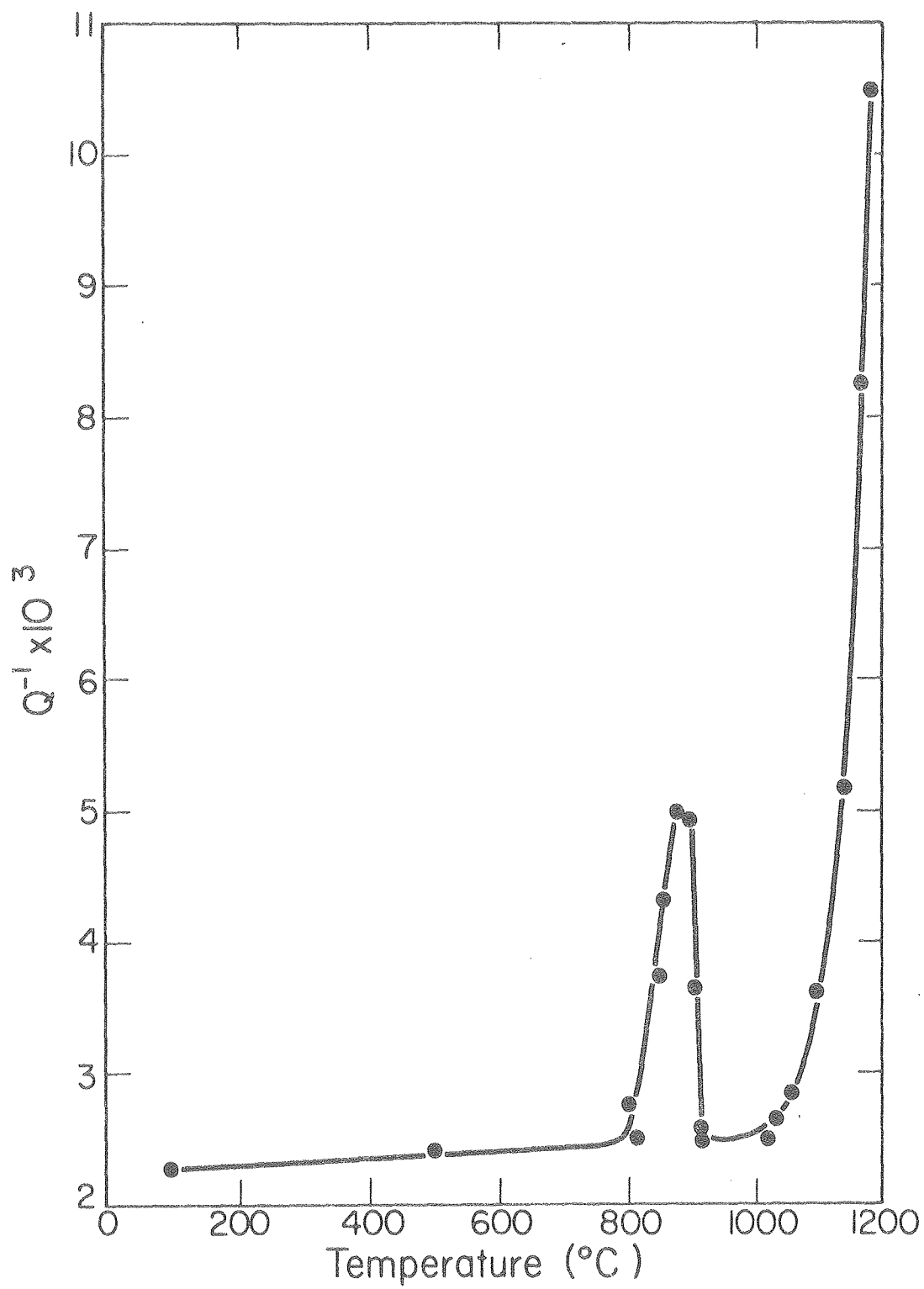
XBL 803-421
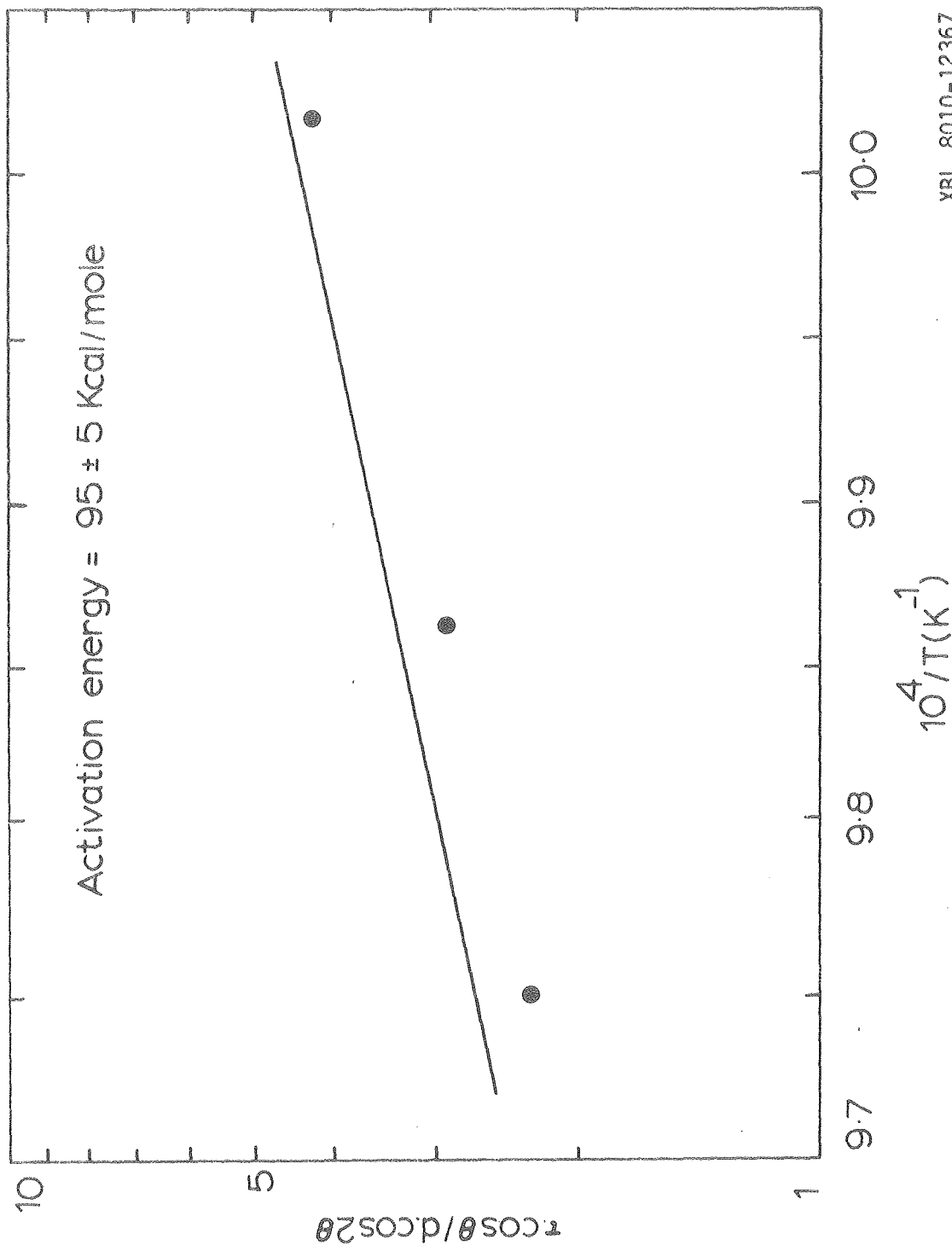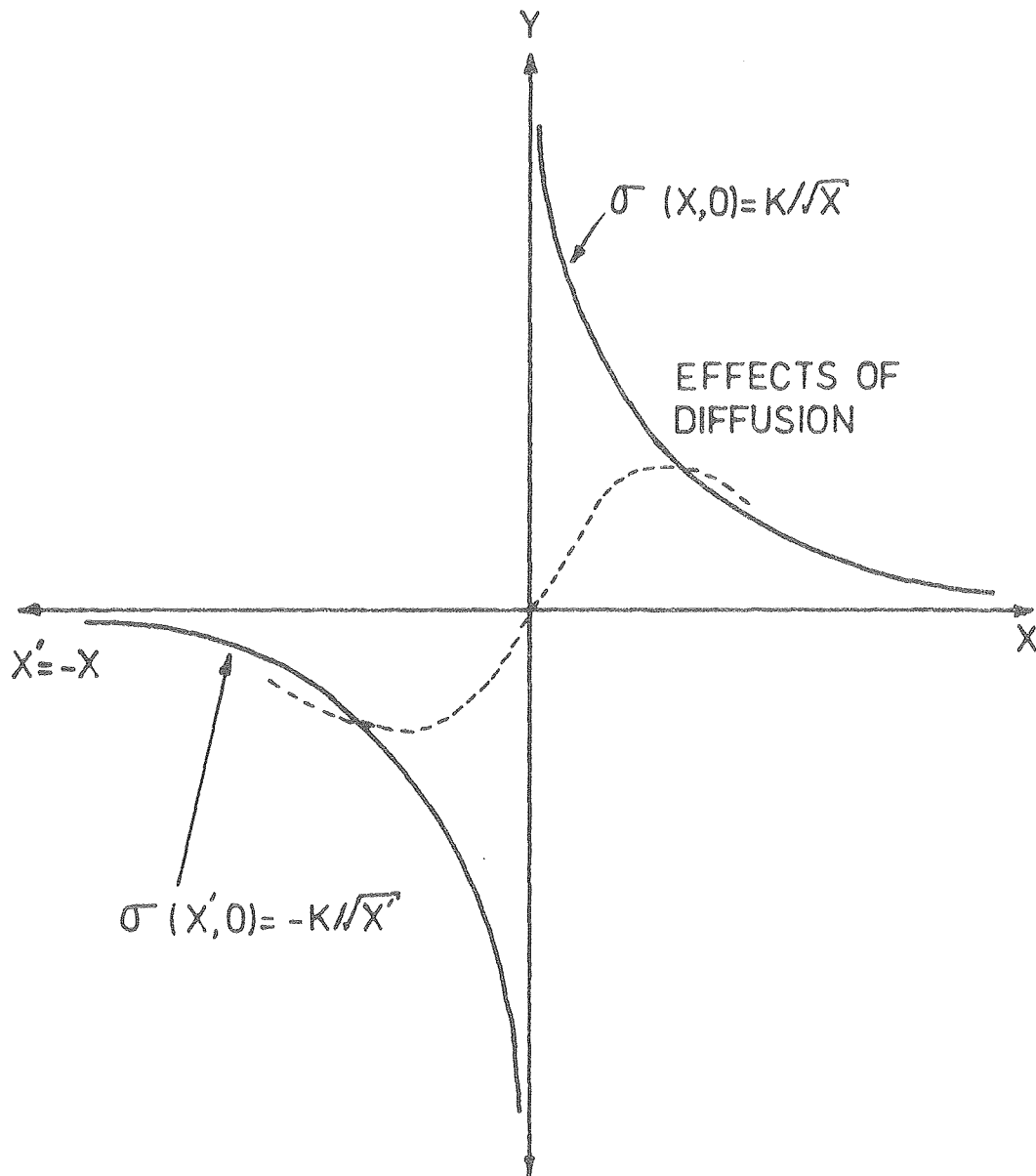
XBL 803-422

Fig. 7-1

Fig. 7-2

XBL 8010-12366

Fig. 7-3

XBL 8010-12367

SLIDING
BOUNDARIES
(MODE II
CRACKS)

σ_∞

$\sigma = K/\sqrt{x}$

X

σ_∞

d

XBL 809-11676

Fig. 8-1

Fig. 8-2

$$q(x,t) \, x^{1/2}/K = f(\alpha t/x^3)$$

$\alpha t/x^3$
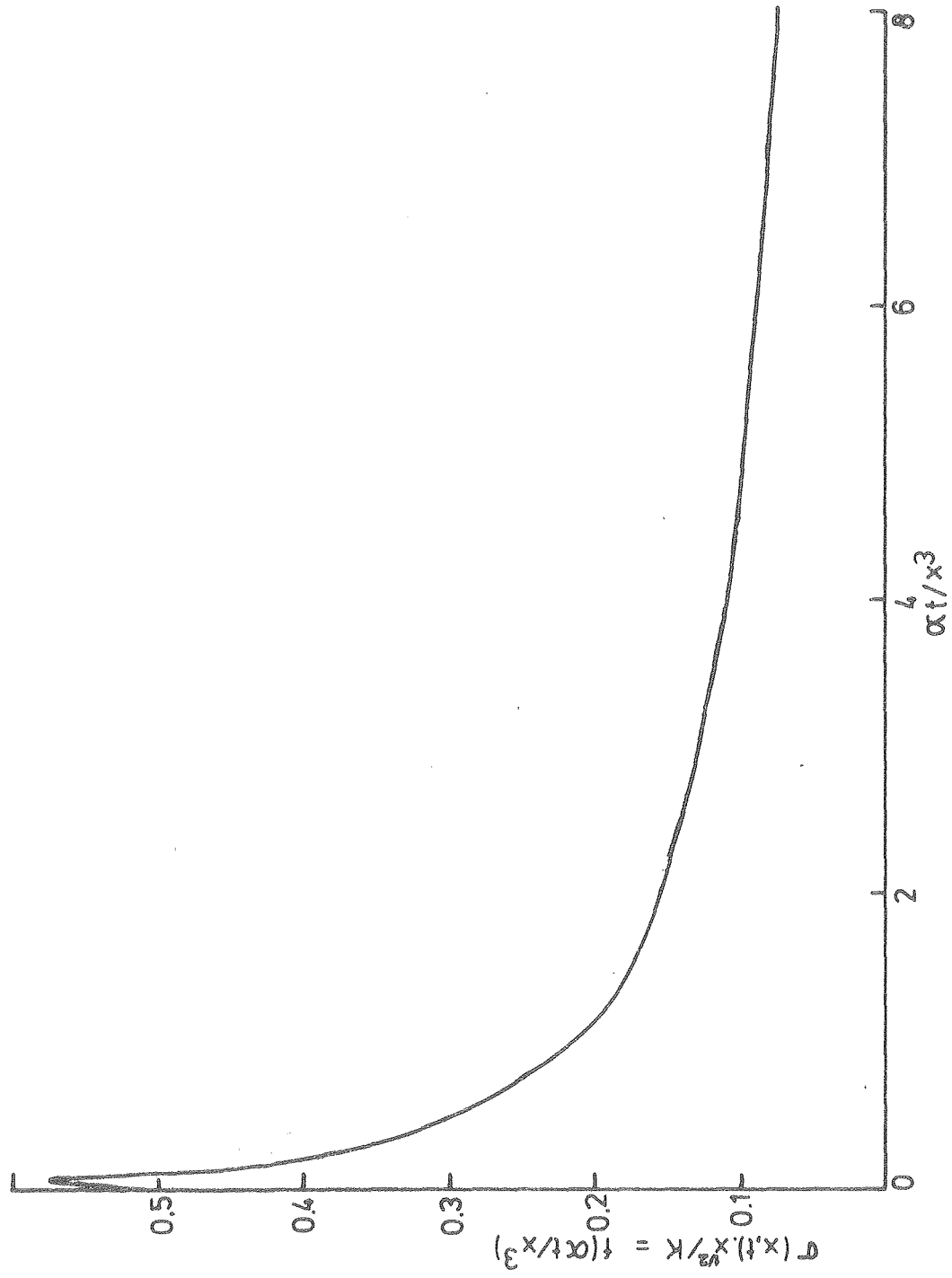
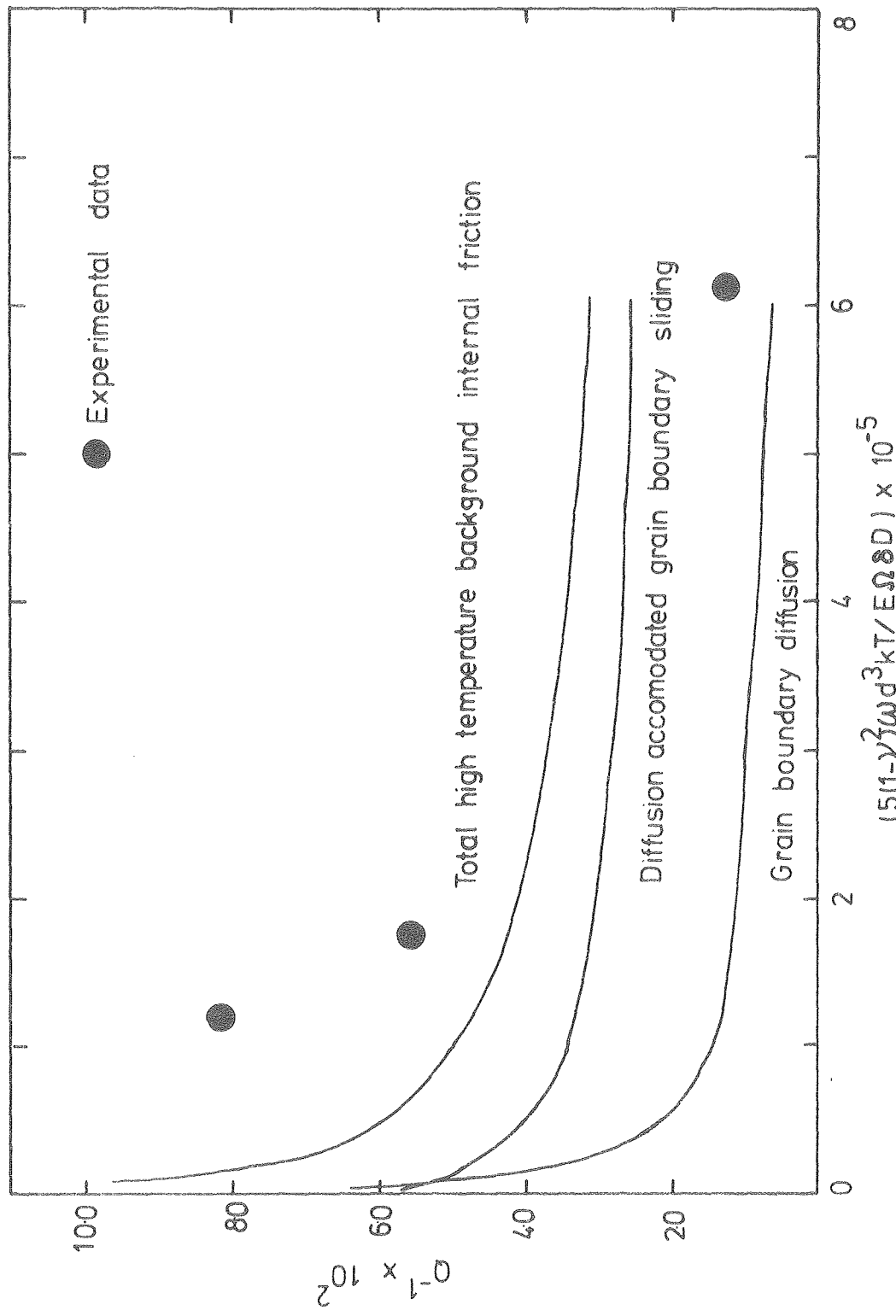Fig. 8-3

XBL 809-11678

Fig. 8-4

XBL 809-11782

$\sigma_{max} = 0.7 K/(\alpha t)^{1/6}$

RELAXED STRESS DISTRIBUTION

$x/(\alpha t)^{1/3}$

$(\alpha t)^{1/6} \sigma (x,t)/K = H[x/(\alpha t)^{1/3}]$

XBL 809-11679

Fig. 8-5